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# Sewage Treatment Plants

Economic Evaluation of Innovative Technologies for Energy Efficiency

Editors: Katerina Stamatelatou and Konstantinos P. Tsagarakis



$$E E^0 0.059 log red / ox (37)$$

For  $O_2$  reduction to  $O_2^{\dagger}$  ( $[O_2]$  1.2 mM) this leads to equations (38) (40).

$$E E^0 0.059 \log[O_2^{\dagger} / O_2] E^0 0.059 \log O_2 0.059 \log[O_2^{\dagger}]$$
 (38)

E 
$$0.18 0.059 \times 2.92 0.059 \log[O_2^{\dagger}]$$
 (39)

E 0.35 0.059 
$$log[O_2^{\dagger}]$$
 (i.e.,  $E^0[O_2]/[O_2^{\dagger}]$  0.35V for a saturated oxygen solution) (40)

Aqueous ozone solutions are unstable. Many effects contribute to this instability, but not all of them are fully elucidated. In basic solutions, ozone is especially unstable. This is due to the formation of  $^{\dagger}OH$  by OH (Chapter 11) and the reaction of  $^{\dagger}OH$  with ozone (Chapter 13). This reaction proceeds even in neutral solutions, where the OH concentration is very low (1 × 10  $^{7}$  M). Acidification and the addition of  $^{\dagger}OH$  scavengers such as bicarbonate further increase the ozone stability in aqueous solutions. In acid solutions and at 31°C, the rate constant of ozone decomposition has been reported at 3 × 10  $^{6}$  s  $^{1}$  (E<sub>a</sub> 82.5 + 8.0 kJ mol  $^{1}$ ) (Sehested et al., 1992). Mechanistic details of the spontaneous decomposition are not yet fully understood.

In natural waters, the dissolved organic matter (DOM) contributes significantly to ozone decay, and waters that have a low DOM and high bicarbonate content show relatively high ozone stability (Chapter 3), which is of relevance for the disinfection efficiency of ozone (Chapter 4).

In micropollutant abatement, for example, the reactivity of a micropollutant determines the efficiency of its elimination by an ozone treatment. Ozone rate constants may vary 8 10 orders of magnitude even within one group of compounds. Cases in point are olefins (Chapter 6) and aromatic compounds (Chapter 7) and also compounds which carry C H functions as only ozone-reactive sites (Chapter 10). In general, ozone rate constants depend on temperature, but there are only very few cases, where details have been measured. The temperature dependence of the second order rate constants can be expressed by the Arrhenius equation [A: pre-exponential factor,  $E_a$ : Activation energy, R: Universal gas constant, T: absolute temperature (K)] (41).

$$k \quad A \times e^{\frac{E_a}{RT}} \tag{41}$$

To determine the parameters A and  $E_{a}$ , equation (41) can be logarithmised, yielding equation (42).

$$\log k \quad \log A \quad \frac{1}{2.3} \frac{E_a}{RT} \tag{42}$$

A plot of log k versus 1/T allows the determination of log A and E<sub>a</sub>. Available data are compiled in Table 2.4 and some plots are shown in Chapters 9 and 10.

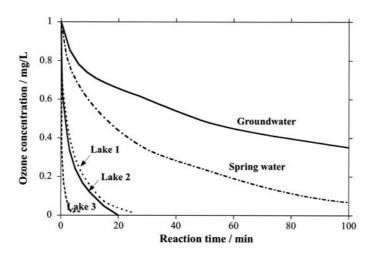
All these compounds react only slowly with ozone. For the more reactive ones, much lower activation energies are expected and hence the temperature dependence of the rate constants will be less pronounced.

There may be a dramatic effect of pH when the site of ozone attack can be deprotonated/protonated, such as in the case of phenols/amines or inorganic ions (Chapters 7, 8, 11 and 12).

# Ozone kinetics in drinking water and wastewater

In these reactions, the aromatic DOM subunits are not yet mineralised but only hydroxylated. This is the likely reason why <sup>†</sup>OH generation does not cease during ozonation even at elevated ozone doses. In addition, other moieties of DOM such as aliphatic CZH bonds also lead to superoxide and eventually <sup>†</sup>OH through the above reactions (see below and Chapter 14). These reactions also apply to DOM in drinking waters.

Figure 3.1 shows the ozone stability in five Swiss waters with various compositions (DOC and alkalinity).



igure . Stability of ozone in various Swiss natural waters at pH 8 and 15°C (ozone dose 1 mg/L). Water quality data: Groundwater (DOC 0.7 mg/L, carbonate alkalinity 6.7 mM); Spring water (DOC 0.9 mg/L, carbonate alkalinity 5.4 mM); Lake 1 (DOC 1.3 mg/L, carbonate alkalinity 2.5 mM); Lake 2 (DOC 1.6 mg/L, carbonate alkalinity 3.6 mM); Lake 3 (DOC 3.2 mg/L, carbonate alkalinity 3.4 mM). From Urfer **et al.**, 2001 with permission.

At pH 8, ozone stability decreases in the sequence groundwater . spring water . lake water 1, 2 . lake water 3. This corresponds to an increasing trend in DOC concentration and a decreasing trend in alkalinity. Ozone has a very similar stability in lake waters 1 and 2, even though the DOC is higher in lake water 2. Carbonate alkalinity which has a stabilising effect on ozone is, however, higher in lake water 2. The effect of carbonate alkalinity has been systematically tested in Lake Zurich water, by varying the carbonate/bicarbonate concentration from 0 to 2.5 mM at pH 8. While keeping the DOC constant, an increase in carbonate alkalinity leads to a significantly lower rate of ozone decomposition (Elovitz et al., 2000a).

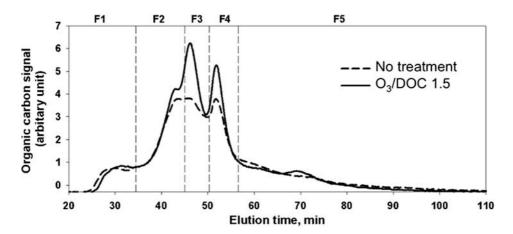
In a survey of eleven DOM isolates, a hundredfold variation of the approximate pseudo-first-order rate constant,  $k_{DOC}$ , for the ozone decrease was observed for synthetic waters containing 2 mg/L of the DOM isolate and 2.5 mM HCO<sub>3</sub> at pH 7 (Figure 3.2) (Elovitz et al., 2000b). This figure shows that Suwannee River fulvic and especially humic acids are outliers and do not represent ozone consumption kinetics of typical DOM in surface waters. Therefore, results from the wide application of these sources of organic matter to simulate drinking water ozonation have to be interpreted with caution and do not allow generalisations on other water sources.

## Ozone kinetics in drinking water and wastewater

To reflect the continuum of the reactive moieties in DOM, the reactivity of ozone with DOM can conceptually be described by a model in which DOM is divided into, for example, five classes of compounds with second-order rate constants ranging from 10 to 10  $^7$  M  $^1$ s  $^1$  (Buffle et al., 2006a). For a wastewater, these individual moieties were assigned with fictitious concentrations in the range between 10 and 70  $\mu$ M. With this approach it was possible to describe the ozone decrease in a particular wastewater (Buffle et al., 2006a). A similar approach allowed the modelling of reactions occurring in a bubble column (Nöthe et al., 2010).

Gel permeation chromatography (GPC), also called size exclusion chromatography (SEC), has been widely used for the determination of the distributions of molecular weights of the DOMs in various waters. In brief, a solution of the analyte (here DOM) is injected onto a chromatographic column containing the separation gel. Low-molecular-weight material can penetrate into the pores of the gel, wherefrom it is eluted slowly while high-molecular-weight material that cannot penetrate the pores elutes faster. Lacking exact reference material, it is not possible to correlate a given retention time with the exact molecular weight of that fraction, but the order of elution, high-molecular-weight material first, low-molecular-weight material later will continue to be approximately correct. In wastewater, for example, the various GPC fractions have a different specific UV absorbance (SUVA). This is a clear indication, that one deals with polymers of different chemical properties and that the above caveat as to the uncertainties of the molecular weights of the various fractions is justified.

The development of detection systems that record not only UV absorbance but also DOC have been essential for the present topic (Huber et al., 1990; Huber & Frimmel, 1991; Huber & Frimmel, 1996; Her et al., 2002). Figure 3.5 shows an example of a SEC-OCD chromatogram of a wastewater before and after ozonation.



igure . Changes in the SEC-OCD chromatogram due to ozonation of 8- $\mu$ m-filtered secondary effluent of the Kloten-Opfikon wastewater treatment plant (Switzerland). SEC-OCD chromatogram before and after ozonation (specific ozone dose 1.5 gO<sub>3</sub>/g DOC). Regensdorf wastewater: TOC 5 mg/L, DOC 4.7 mg/L, HCO<sub>3</sub> 2.86 mM, pH 7.0. F1, Biopolymers; F2, Humics; F3, Building blocks; F4, Low-molecular-weight humics and acids; F5, Low-molecular-weight neutrals (Lee & von Gunten, unpublished).

# Chemistry of Ozone in Water and Wastewater Treatment

Irrespective of the origin of a water, there are always various partially-separated fractions detected. In natural waters and wastewaters, there is barely a fraction that may be associated with really low-molecular-weight material (, 150 Da). SEC-OCD chromatograms of natural waters, drinking waters, soluble microbial products and wastewater have been published (Fuchs, 1985a, b, c; Allpike et al., 2005; Meylan et al., 2007; Jiang et al., 2010). As expected, waters from different origins such as groundwaters, surface waters and wastewaters show substantial differences. Waters contained in barrages that are fed by nutrients from nearby agricultural activities may be rich in extracellular organic matter (EOM) of algae (Hoyer et al., 1985) or groundwaters in peaty areas may be enriched in humics. Such differences are reflected in differences in ozone reactivity (Figure 3.2) but (obviously) also in SEC-OCD chromatograms. Common study objects are fulvic and humic acids, and data as to their structures are becoming increasingly available (Reemtsma & These, 2005; Reemtsma et al., 2006a, b, 2008; These & Reemtsma, 2003, 2005; These et al., 2004)

Figure 3.6 shows the changes of the various DOM fractions caused by ozone reactions. The so-called hydrophobic DOM fraction is retained by the chromatographic column, that is, not the entire DOC is accounted for by SEC-OCD.

igure . Changes in the SEC-OCD chromatogram due to ozonation of 8- $\mu$ m-filtered secondary effluent of the Kloten-Opfikon wastewater treatment plant (Switzerland). Changes of individual fractions (mgC/L) for various specific ozone doses between 0.25 1.5 gO<sub>3</sub>/gDOC. Regensdorf wastewater: TOC 5 mg/L, DOC 4.7 mg/L, HCO<sub>3</sub> 2.86 mM, pH 7.0. F1, Biopolymers; F2, Humics; F3, Building blocks; F4, Low-molecular-weight humics and acids; F5, Low-molecular-weight neutrals (Lee & von Gunten, unpublished).

The hydrophobic fraction can be determined from the difference between measured DOC and the sum of all fractions. This hydrophobic fraction decreases significantly with increasing ozone dose. This means that this part of DOC becomes detectable upon ozone treatment as fractions denoted building blocks and low-molecular-weight humics and acids. The higher molecular weight fractions biopolymers and humics are only marginally changed. Note that at the very high ozone dose of 7.5 mg/L only about 10% of the DOM-DOC is converted to low-molecular-weight compounds.

The specific ozone doses in Figures 3.5 and 3.6 are given on a  $gO_3/gDOC$  basis. This unit has been chosen, because it is very practical for water treatment purposes, notably in wastewaters (Hollender et al., 2009).

# Ozone kinetics in drinking water and wastewater

Table . Compilation of ozone and \*OH rate constants (unit: M  $^1$ s  $^1$ ) of selected ozone-refractory micropollutants in drinking water and wastewater at pH 7

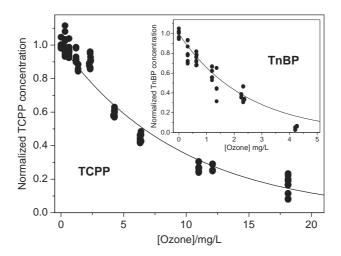
ompound	Source/application	k o one	k •	eference
Atrazine	Herbicide	6	3 × 10 <sup>9</sup>	Acero <b>et al</b> ., 2000
Iopromide	X-ray contrast agent	, 0.8	$3.3 \times 10^9$	Huber <b>et al</b> ., 2003
Diazepam	Tranquiliser	0.75	$7.2 \times 10^9$	Huber <b>et al</b> ., 2003
NDMA	Oxidation by-product	5 <b>x</b> 10 <sup>2</sup>	$4.5 \times 10^{8}$	Lee <b>et al</b> ., 2007a
Tris-(2-chloro-isopropyl) phosphate (TCPP)	Flame retardant	1	7 × 10 <sup>8</sup>	Pocostales <b>etal</b> ., 2010
Tris-(2-chloro-ethyl) phosphate (TCEP)	Flame retardant	1	$7.4 \times 10^8$	Watts & Linden, 2009
Tri- <b>n</b> -butyl phosphate (TnBP)	Plasticiser	1	2.8 <b>x</b> 10 <sup>9</sup>	Pocostales <b>etal</b> ., 2010

For the elimination of ozone-refractory micropollutants, one may write the competing reactions (23) and (24), where M denotes the water matrix (DOC plus bicarbonate, see above) and P the micropollutant.

$$M ^{\dagger}OH M-ox (23)$$

$$P ^{\dagger}OH P-ox (24)$$

The <sup>†</sup>OH scavenging rate that determines the rate of reaction (24) and <sup>†</sup>OH yields (in wastewater) has been given above. Based on this, the elimination efficiency of a given ozone-refractory micropollutant can be calculated. This is shown in Figure 3.14 for two organic phosphates.



igure . Experimental data (symbols) and simulation (solid lines) of the degradation of TCPP and TnBP (inset) in diluted Neuss wastewater (DOC 5.5 mg/L). Reprinted with permission from Pocostales **et al.**, 2010. Copyright (2010) American Chemical Society.

### Ozone kinetics in drinking water and wastewater

that the addition of H<sub>2</sub>O<sub>2</sub> allows a higher degree of transformation for a given hydraulic residence time. The extent of transformation has to be compared for the complete depletion of ozone in the absence and presence of H<sub>2</sub>O<sub>2</sub>. In the surface water, the overall extent of transformation is fairly similar for both scenarios, whereas in the groundwater, H<sub>2</sub>O<sub>2</sub> addition improves the elimination of pCBA from about 40 to 65%. Thus, depending on water quality, a similar or only small increase of the extent of transformation is observed in presence of  $H_2O_2$ .

## U photolysis of o one

In his pioneering work, Taube concluded that only H<sub>2</sub>O<sub>2</sub> is formed upon the photolysis of ozone in water (Taube, 1957). This conclusion was based on the apparent 1:1 stoichiometry of ozone consumption and H<sub>2</sub>O<sub>2</sub> formation in the presence of acetate as an <sup>†</sup>OH scavenger. At this time, it was not yet known that in its  $^{\dagger}$ OH-induced reactions in the presence of O<sub>2</sub>, acetate gives rise to relatively large amounts of H<sub>2</sub>O<sub>2</sub> (Schuchmann et al., 1985). Later on, when it was realised that <sup>†</sup>OH radicals are generated in this reaction, the ozone/UV system was widely discussed among potential AOPs (Glaze et al., 1982; Peyton et al., 1982; Peyton & Glaze, 1987, 1988; Takahashi, 1990; Gurol & Vatistas, 1987; Ikemizu et al., 1987; Morooka et al., 1988). The reactions in this rather complex system are now reasonably well understood (Reisz et al., 2003).

Upon photolysis, ozone is decomposed into  $O_2$  and oxygen atoms  $O(^{1}D)$  (excited state) and  $O(^{3}P)$ (ground state) (Wayne, 1987; Schriver-Mazzuoli, 2001; Bauer et al., 2000; Smith et al., 2000; Taniquchi et al., 2000). In the gas phase and below 300 nm, the main processes (quantum yield, reactions (27) and (28), that is, the formation of  $O(^1D)$  and singlet oxygen,  $O_2(^1_g)$ , as well as oxygen in its ground state,  $O_2(^3_g)$ ). Reactions that yield  $O(^3P)$  [reactions (29) and (30)] are of lower importance 0.1) (Wayne, 1987; Hancock & Tyley, 2001; Wine & Ravishankara, 1982).

$$O_3$$
 hn  $O(^1D)$   $O_2(^1D_g)$  (27)

$$O_3$$
 hn  $O(^1D)$   $O_2(^3S_g)$  (28)  
 $O_3$  hn  $O(^3P)$   $O_2(^1D_g)$  (29)

$$O_3$$
 hn  $O(^3P)$   $O_2(^1D_g)$  (29)

$$O_3$$
 hn  $O(^3P)$   $O_2(^3S_g)$  (30)

The quantum yield of O(1D) formation falls to a value near 0.1 above a wavelength of about 320 nm but not to zero. This shows that the spin-forbidden formation of  $O(^1D)$  and  $O_2(^3 \text{ g})$  [reaction (28)] is possible (Bauer et al., 2000; Smith et al., 2000; Taniguchi et al., 2000; Jones & Wayne, 1970). O(1D) is very energetic [heat of formation, 437 kJ mol  $^{1}$  (Taniguchi et al., 1999)] and therefore reacts rapidly even with water [reaction (31), k  $^{1.8}$  x  $^{10}$  M  $^{1}$ s  $^{1}$  (Biedenkapp et al., 1970), by insertion (Taube, 1957)].

$$O(^{1}D) H_{2}O H_{2}O_{2}$$
 (31)

In the gas phase, the excess energy of the H<sub>2</sub>O<sub>2</sub> molecule so formed results in the fragmentation of the O O bond [reaction (32); BDE 210 kJ mol (McKay & Wright, 1998)].

$$(H2O2)hot 2 †OH$$
 (32)

Singlet oxygen (40%, Table 6.7) but no  $^{\dagger}$ OH (Flyunt et al., 2003) are formed with Gua derivatives. The latter is surprising as the reduction potential of the guanine riboside Guo is lower (E<sub>7</sub> 1.29 V) than that of adenine riboside Ado (E<sub>7</sub> 1.56 V) (von Sonntag, 2006). This may exclude reaction (7) and favour reaction (8) as the precursor of  $^{\dagger}$ OH.

### E T T

In the reaction of ozone with DNA,  $^{\dagger}$ OH plays an important role (Van der Zee et al., 1987; Theruvathu et al., 2001). This  $^{\dagger}$ OH formation must be due to the reaction of ozone with the adenine moiety (Ishizaki et al., 1984; Theruvathu et al., 2001). For the determination of the intrinsic ozone rate constant with DNA, tertiary butanol has to be added. Under such conditions, the rate of reaction of DNA is only 410 M  $^{1}$ s  $^{1}$  (in the absence of tertiary butanol  $k_{obs}$   $1.1 \times 10^{3}$  M  $^{1}$ s  $^{1}$ ), i.e. much lower than that of the weighted average of the nucleobases. In the case of  $^{\dagger}$ OH, which reacts with the nucleobases and their derivatives at close to diffusion-controlled rates [k  $3 \times 10^{9}$  M  $^{1}$ s  $^{1}$  (Buxton et al., 1988)], the rate constant of  $^{\dagger}$ OH with DNA is considerably lower [k  $2.5 \times 10^{8}$  M  $^{1}$ s  $^{1}$  (Udovicic et al., 1994)], since in this non-homogeneous reaction with the macromolecule DNA two terms, a diffusion term ( $k_{diff}$ ) and a reaction term ( $k_{diff}$ ) have to be considered (Udovicic et al., 1991). The observed overall rate constant ( $k_{obs}$ ) is the harmonic mean of these two rate constants [cf. Equation (9)].

$$\frac{1}{k_{\text{obs}}} \frac{1}{k} \frac{1}{k_{\text{diff}}} \tag{9}$$

In contrast to <sup>†</sup>OH, ozone reacts with the nucleobases at rates much below the diffusion-controlled limit, and the second term must fall away. Hence, the rate of reaction of ozone with the nucleic acids is only given by the first term, that is, it should be close to that of the weighted average of the concentrations of the various nucleobases in the nucleic acid times their rate constants with ozone. This is not observed. The reason for this is as yet not understood. As on this basis, the dAdo moiety can barely contribute (cf. the low rate constant given in Table 6.1) and the explanation that <sup>†</sup>OH production must be due to an ozone reaction with this moiety must fall away. It is tentatively suggested that in double-stranded DNA, hydrogen bonding between the nucleobases and base stacking may be the reason for these unexpected effects.

Inactivation of micro-organisms and toxicological assessment of ozone-induced products

Corresponding experiments with RNA are as yet not available. From the rate constants given in Table 6.1, one would assume that in RNA the guanine moiety is the most likely one to become degraded upon ozone treatment. This has indeed been observed (Shinriki et al., 1981). In DNA, the situation might be somewhat different. Besides guanine, thymine may be the other preferred target.

To assess the disinfection efficiency in water treatment, the CT-concept is applied. C stands for the concentration of disinfectant (ozone) and T for the contact time; CT is the product of the aqueous disinfectant concentration and contact time. In laboratory systems where ozone can be directly measured, the CT can be expressed as ozone exposure. This corresponds to the integral under the ozone decay curve of an ozone vs. time plot (von Gunten & Hoigné, 1994). In real reactor systems, the CT value is not easily accessible. Often, time-resolved ozone concentration profiles and contact times are not readily available. To overcome this problem, several concepts have been developed (Rakness, 2005; Rakness et al., 2005). A conservative approach is the calculation of CT<sub>10</sub>, where C is the reactor effluent concentration (or concentration at last sampling point) and T<sub>10</sub> is the travel time of the first 10% of the water going through the reactor. T<sub>10</sub> is typically much shorter than the hydraulic retention time ; the T<sub>10</sub>/ ratio is often around 0.5 (Roustan et al., 1993). This approach does not take into consideration that the ozone concentration is significantly higher near the influent of the reactor, and ozone exposure is underestimated. Especially for ozone-resistant micro-organisms such as C. parvum oocysts (Table 4.1), this approach may lead to higher required ozone doses and hence to an increased formation of disinfection by-products such as bromate (Chapters 11 and 14). To make a better approximation of the real ozone concentration in the reactor, calculating the geometric mean of the ozone concentrations at the inlet and outlet [C  $(C_{in} \times C_{out})^{0.5}$ ] has been suggested (Rakness et al., 2005). This method is an improvement compared to the standard CT<sub>10</sub> approach. Yet, it is still far from the real ozone exposure. To further improve the prediction of disinfection efficiency, combined models including reactor hydraulics (determined by tracer experiments), ozone decay kinetics and disinfection kinetics have to be used (Roustan et al., 1993; von Gunten et al., 1999; Do-Quang et al., 2000; Gallard et al., 2003; Kim et al., 2004; Smeets et al., 2006). To include the variability of parameters such as inactivation rate constant, CT<sub>lag</sub>, ozone decay rate, temperature, changes in water quality and hydraulics, uncertainty modelling is a powerful tool for assessing the variability in the disinfection efficiency (Neumann et al., 2007). With increasing computing power, methods based on computational fluid dynamics can make even more accurate predictions and are a valuable tool in reactor design (Wols et al., 2010).

In wastewater, ozone decay is typically too fast for using measured ozone concentrations to calculate CT values (Chapter 5). Parameters for process design in wastewater disinfection by ozone have been discussed (Xu et al., 2002).

The abatement of organic micropollutants during ozonation does typically not lead to their mineralisation but to the formation of transformation products (Huber et al., 2004; McDowell et al., 2005; Radjenovic et al., 2009; Benner & Ternes, 2009a, b; Dodd et al., 2010; Lange et al., 2006; Schumacher et al., 2004a). Thus, ozonation products may contain more or fewer structural similarities to the original

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compounds, and the question arises, whether the original biological effects (e.g. antimicrobial activity, oestrogenicity, herbicidal properties, etc.) are lost even when the molecules are only slightly modified. There is also some concern about new biological effects resulting from the transformation of micropollutants. Since these questions can rarely be answered by elucidating the structures of the transformation products only, ozonated solutions of a biologically active compound may have to be tested for remaining or new biological activity (Mestankova et al., 2011; Escher & Fenner, 2011). In the following, some of the most important classes of biologically active compounds and the change in biological activity upon ozonation will be discussed.

Compounds behaving like hormones and disturbing the hormonal status of an organism are called endocrine disrupting compounds (EDCs). Among many other bioactive compounds, they are considered the most important class in terms of adverse effects to aquatic life (Runnalls et al., 2010). The general implication for the water industry of the presence of EDCs and other micropollutants and their removal has been addressed (Snyder et al., 2003, 2006; Broséus et al., 2009). The simplest way to disturb the hormonal system of an organism is to interact with a receptor in a way similar to the hormone itself. The receptor of the female hormone oestrone is a typical example and is called an oestrogen receptor, because it also binds other oestrogenic compounds such as the natural hormone oestradiol and the synthetic hormone 17 -ethinyloestradiol. These oestrogenic compounds are phenols, and the phenolic group is essential for binding to the oestrogen receptor (Lee et al., 2008). They are found in WWTP effluents in concentrations of up to several ng/L (Andersen et al., 2003; Ning et al., 2007a). One of the main concerns of the release of oestrogenic compounds is the feminisation of male fish (Sumpter & Johnson, 2008). In an experimental lake in north-western Ontario, Canada, the fish population was almost extinct after a seven-year exposure to 5 6 ng/L 17 -ethinyloestradiol (Kidd et al., 2007).

Besides the phenol function, there are hydrophobic binding sites that influence the equilibrium constant of equilibrium (10).

Because of structural similarities to oestrogenic compounds, many industrial and natural compounds can also bind to oestrogen receptors with different equilibrium constants of equilibrium (10) and hence exert different endocrine disrupting potentials (Bonefeld-Jörgensen et al., 2007). A critical review on in vitro and in vivo effects of synthetic organic chemicals including phenol-containing compounds is available (Tyler et al., 1998). Some examples of such compounds will be discussed in the following.

Bisphenol A, t-butylphenol, octylphenol and nonylphenol are technical products and abundant in wastewaters and surface waters (Ahel et al., 1994; Voutsa et al., 2006; Ning et al., 2007a).

They differ by orders of magnitude in their binding constants and hence in their endocrine disrupting potential. The daily intake of nonylphenols by food has been estimated at 7.5 µg for an adult in Germany (Günther, 2002). This high value indicates that drinking water may not be the major source of EDCs to man, but the main concern of these EDCs is related to their adverse effects on aquatic life (Oehlmann et al., 2000, 2006; Kidd et al., 2007; Sumpter & Johnson, 2008). Nonylphenols lead to feminisation of aquatic organisms and a decrease in male fertility and the survival of juveniles at concentrations below 10 µg/L (Soares et al., 2008). Prosobranch snails have been suggested as test organisms (Duft et al., 2007; Oehlmann et al., 2007). For a comparison of prosobranch snails and fish see Jobling et al. (2004). Similar concerns are related to bisphenol A. Its mode of action and potential human health effects have been reviewed (Vandenberg et al., 2009).

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As there are so many different compounds that give rise to endocrine disrupting activity, in vivo and in vitro test systems have been developed to assess water samples experimentally. Two test systems that are widely used for in vivo and in vitro oestrogenicity assessment are based on in vivo measurement of the blood plasma vitellogenin (VTG) concentrations in male rainbow trout (Oncorhynchus mykiss) and in vitro measurement of the oestrogen binding to a human oestrogen receptor (yeast oestrogen screen, YES) [for a review see (Sumpter & Johnson, 2008), for some recent developments requiring shorter reaction times (LYES) see (Schultis & Metzger, 2004)]. For the YES assay, two plasmids have been introduced into a yeast cell. The first plasmid generates the human -oestrogen receptor. Upon addition of the EDC to be tested, it binds to the receptor according to equilibrium (10) and changes its structure. This receptor complex now binds to the second plasmid and triggers the formation of a marker enzyme. The resulting enzyme activity is measured. In these assays, bisphenol A and the mixture of technical nonylphenols are about four orders of magnitude less potent than oestradiol.

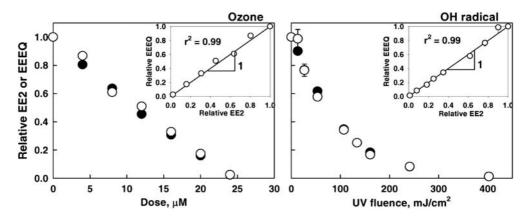
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confirmed for E2 and EE2 (Linden et al., 2007). Other oxidants such as chlorine, bromine, chlorine dioxide and ferrate (VI) also efficiently destroy the oestrogenicity of EE2 (Lee et al., 2008).



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A considerable number of EDCs have been detected in WWTPs (Spengler et al., 2001). In many WWTPs, oestrogenicity is controlled by oestrogenic compounds (E1, E2 and EE2) with concentrations in the ng/L range rather than industrial compounds such as alkylphenols, alkylphenolmonoethoxylates and alkylphenoldiethoxylates, even though present in g/L levels (Aerni et al., 2004). However, this might be different in WWTPs with a high contribution of industrial wastewater. Oestrogenicity in wastewater is eliminated well by activated sludge processes (. 90% removal) (Escher et al., 2009). Since many EDCs are phenols, they are readily eliminated by an ozonation step and lose their hormonal activity upon attack by chemical oxidants (see above). This was demonstrated in a full-scale WWTP in Switzerland where a . 95% elimination of oestrogenicity (YES assay) was found upon ozonation (Escher et al., 2009). In another study, the oestrogenicity was reduced by 90% for an ozone dose of about 0.4 mgO<sub>3</sub>/mg DOC (Stalter et al., 2011). The effective removal of oestrogenic activity by ozonation has been confirmed by an additional test with yolk-sac larvae (Stalter et al., 2010b). A significant reduction of vitellogenin levels was observed in fish exposed to ozonated wastewater compared to fish reared in conventionally treated wastewater.

In other WWTPs, oestrogenicity (YES assay) decreases in parallel to the degradation of bisphenol A by ozone (Figure 4.3).

The same effect is also apparent in the effluent of two other WWTPs where bisphenol A and EEQ were 10% (Köln-Stammheim) and 1% (Bottrop) of the given example. In these wastewaters, there is a very close correlation between the presence of the technical product bisphenol A and oestrogenicity. This points to the predominance of industrial sources (contraceptives were below detection) for the observed oestrogenicity in these wastewaters. However, bisphenol A and alkylphenols (data not shown) can only account for about 10% of the observed oestrogenicity. Therefore, there must be other, as yet unknown, oestrogenic

Singlet oxygen (40%, Table 6.7) but no  $^{\dagger}$ OH (Flyunt et al., 2003) are formed with Gua derivatives. The latter is surprising as the reduction potential of the guanine riboside Guo is lower (E<sub>7</sub> 1.29 V) than that of adenine riboside Ado (E<sub>7</sub> 1.56 V) (von Sonntag, 2006). This may exclude reaction (7) and favour reaction (8) as the precursor of  $^{\dagger}$ OH.

### E T T

In the reaction of ozone with DNA,  $^{\dagger}$ OH plays an important role (Van der Zee et al., 1987; Theruvathu et al., 2001). This  $^{\dagger}$ OH formation must be due to the reaction of ozone with the adenine moiety (Ishizaki et al., 1984; Theruvathu et al., 2001). For the determination of the intrinsic ozone rate constant with DNA, tertiary butanol has to be added. Under such conditions, the rate of reaction of DNA is only 410 M  $^{1}$ s  $^{1}$  (in the absence of tertiary butanol  $k_{obs}$   $1.1 \times 10^{3}$  M  $^{1}$ s  $^{1}$ ), i.e. much lower than that of the weighted average of the nucleobases. In the case of  $^{\dagger}$ OH, which reacts with the nucleobases and their derivatives at close to diffusion-controlled rates [k  $3 \times 10^{9}$  M  $^{1}$ s  $^{1}$  (Buxton et al., 1988)], the rate constant of  $^{\dagger}$ OH with DNA is considerably lower [k  $2.5 \times 10^{8}$  M  $^{1}$ s  $^{1}$  (Udovicic et al., 1994)], since in this non-homogeneous reaction with the macromolecule DNA two terms, a diffusion term ( $k_{diff}$ ) and a reaction term ( $k_{diff}$ ) have to be considered (Udovicic et al., 1991). The observed overall rate constant ( $k_{obs}$ ) is the harmonic mean of these two rate constants [cf. Equation (9)].

$$\frac{1}{k_{\text{obs}}} \frac{1}{k} \frac{1}{k_{\text{diff}}} \tag{9}$$

In contrast to <sup>†</sup>OH, ozone reacts with the nucleobases at rates much below the diffusion-controlled limit, and the second term must fall away. Hence, the rate of reaction of ozone with the nucleic acids is only given by the first term, that is, it should be close to that of the weighted average of the concentrations of the various nucleobases in the nucleic acid times their rate constants with ozone. This is not observed. The reason for this is as yet not understood. As on this basis, the dAdo moiety can barely contribute (cf. the low rate constant given in Table 6.1) and the explanation that <sup>†</sup>OH production must be due to an ozone reaction with this moiety must fall away. It is tentatively suggested that in double-stranded DNA, hydrogen bonding between the nucleobases and base stacking may be the reason for these unexpected effects.

Inactivation of micro-organisms and toxicological assessment of ozone-induced products

Corresponding experiments with RNA are as yet not available. From the rate constants given in Table 6.1, one would assume that in RNA the guanine moiety is the most likely one to become degraded upon ozone treatment. This has indeed been observed (Shinriki et al., 1981). In DNA, the situation might be somewhat different. Besides guanine, thymine may be the other preferred target.

To assess the disinfection efficiency in water treatment, the CT-concept is applied. C stands for the concentration of disinfectant (ozone) and T for the contact time; CT is the product of the aqueous disinfectant concentration and contact time. In laboratory systems where ozone can be directly measured, the CT can be expressed as ozone exposure. This corresponds to the integral under the ozone decay curve of an ozone vs. time plot (von Gunten & Hoigné, 1994). In real reactor systems, the CT value is not easily accessible. Often, time-resolved ozone concentration profiles and contact times are not readily available. To overcome this problem, several concepts have been developed (Rakness, 2005; Rakness et al., 2005). A conservative approach is the calculation of CT<sub>10</sub>, where C is the reactor effluent concentration (or concentration at last sampling point) and T<sub>10</sub> is the travel time of the first 10% of the water going through the reactor. T<sub>10</sub> is typically much shorter than the hydraulic retention time ; the T<sub>10</sub>/ ratio is often around 0.5 (Roustan et al., 1993). This approach does not take into consideration that the ozone concentration is significantly higher near the influent of the reactor, and ozone exposure is underestimated. Especially for ozone-resistant micro-organisms such as C. parvum oocysts (Table 4.1), this approach may lead to higher required ozone doses and hence to an increased formation of disinfection by-products such as bromate (Chapters 11 and 14). To make a better approximation of the real ozone concentration in the reactor, calculating the geometric mean of the ozone concentrations at the inlet and outlet [C  $(C_{in} \times C_{out})^{0.5}$ ] has been suggested (Rakness et al., 2005). This method is an improvement compared to the standard CT<sub>10</sub> approach. Yet, it is still far from the real ozone exposure. To further improve the prediction of disinfection efficiency, combined models including reactor hydraulics (determined by tracer experiments), ozone decay kinetics and disinfection kinetics have to be used (Roustan et al., 1993; von Gunten et al., 1999; Do-Quang et al., 2000; Gallard et al., 2003; Kim et al., 2004; Smeets et al., 2006). To include the variability of parameters such as inactivation rate constant, CT<sub>lag</sub>, ozone decay rate, temperature, changes in water quality and hydraulics, uncertainty modelling is a powerful tool for assessing the variability in the disinfection efficiency (Neumann et al., 2007). With increasing computing power, methods based on computational fluid dynamics can make even more accurate predictions and are a valuable tool in reactor design (Wols et al., 2010).

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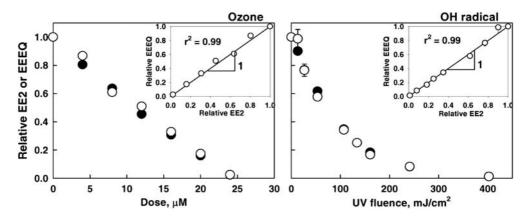
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	cal test results from <b>n</b> and a	and <b>n t</b> r tests on sec	condary effluents treated
Treatment system	Test systems	esults	eferences
Ozonation of	Fish early life stage toxicity	Development retardation	Stalter <b>et al</b> ,

Effect disappears after

post-sand filtration Removal of oestrogenicity 2010b

test (rainbow trout,

m ss

secondary effluent

Toxicity is not as well-defined as, for example, endocrine disruption. Endocrine disruption can be well-described by a relatively simple assay, for example, the YES assay that provides a reasonable answer. Other tests may be used for confirmation, but are not strictly required. In contrast for describing toxicity, many different test systems may have to be utilised depending on the relevant endpoints for ecosystems (Stalter et al., 2010a). Different toxicity tests have been carried out with ozonated wastewater (Table 4.2). For example, the Lumbriculus variegatus test, based on the development of this worm within 28 days, revealed a significantly enhanced toxicity after ozonation compared to conventional treatment (Stalter et al., 2010a). Moreover, a significantly increased genotoxicity was observed, detected with the comet assay using haemolymph of the zebra mussel (Stalter et al., 2010a). The comet assay, originally developed for radiation-induced DNA strand breakage caused by ionising radiation in cells (Ostling & Johanson, 1984), has been later applied to the assessment of DNA-reactive agents (Collins et al., 1997). Also the fish early life stage toxicity test (FELST) using rainbow trout (Oncorhynchus mykiss) revealed a considerable developmental retardation of test organisms exposed to ozonated wastewater (Stalter et al., 2010b). All these effects were removed by subsequent sand filtration to the level of conventional treatment. Activated carbon treatment even resulted in a significant reduction of genotoxicity. The build-up of toxicity upon ozonation and its subsequent removal during post-sand filtration points to the formation of biodegradable organic compounds such as aldehydes and ketones from the reaction of ozone with DOM (Chapter 3). Apparently, these compounds show toxicity in certain test systems but not in others. It is very unlikely that the increased toxicity is caused by transformation products from micropollutants.

The above statement, that toxicity is not a simple parameter, is illustrated by the fact that other parameters that can measure toxicity such as the Lemna minor growth inhibition test and the Chironomid toxicity test did not give a response on ozonated wastewater (Stalter et al., 2010a).

It seems fair to conclude that ozone-induced toxicity is mostly transient and can be eliminated by biological sand filtration or biological activated carbon filtration. Hence, toxicity may not be a major obstacle for introducing ozonation as a polishing step in wastewater treatment.

# Chapter 5

# Integration of ozonation in drinking water and wastewater process trains

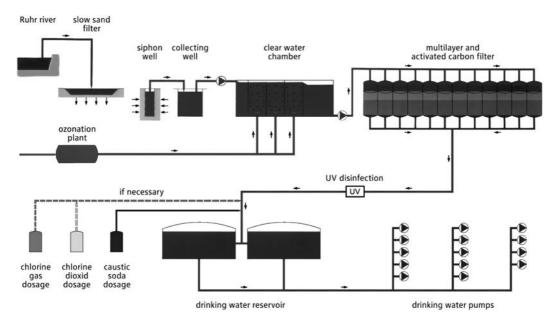
#### ST SPE TS

### . . rinking water

In France, the earliest test with ozonation for disinfection dates back to 1886. In 1906, ozonation for full-scale drinking water disinfection, after slow sand filtration, was installed in Nice (France) (Le Palouë & Langlais, 1999). In the early applications of ozone in water treatment, ozonation was basically a replacement for chlorine disinfection. Especially in water supplies treating groundwater, there was a substantial carryover of ozone into reservoirs and the distribution systems, because in these waters ozone is quite stable due to the low DOC concentration and the high carbonate alkalinity (Chapter 3). In Germany, ozonation of groundwaters and surface waters also started around 1900. Several plants (Wiesbaden, Paderborn, Hermannstadt) were closed down, however, after only a few years of operation, mainly due to the lower costs of chlorination (Böhme, 1999). In the USA, the first ozone installations for taste and odour or colour removal were established in the early 1900s. Significant capacity was only installed in the mid-1980s (Rice, 1999). In other countries such as Japan, Canada, UK, The Netherlands, Belgium and Switzerland, ozone application for drinking water treatment started between the 1940s and the 1960s (Matsumoto & Watanabe, 1999; Lowndes, 1999; Kruithof & Masschelein, 1999; Geering, 1999; Larocque, 1999). A compilation of the estimated number of drinking water treatment plants in Europe and North America is shown in Table 5.1. From this comparison, it is evident that the number of ozonation plants per capita is very high in France and Switzerland, whereas it is rather low in the USA and Japan. This reflects the high affinity of many water suppliers to chlorine and related products, despite the many disadvantages of these oxidants compared to ozone (Sedlak & von Gunten, 2011).

# . . Municipal wastewater

So far, there is only a limited number of wastewater treatment plants that use ozonation. Most of these plants are located in Canada, Germany, Japan, South Korea and the USA (Paraskeva & Graham, 2002) with the main objective of disinfection. Disinfection of wastewater effluent is mandatory in some states in the USA. In Europe, it is only applied occasionally for achieving bathing water quality goals. Disinfection of wastewaters is typically also applied for irrigation or other reuse purposes. Disinfection of wastewaters, however, is often achieved with chlorine or UV rather than ozone. Nevertheless, the growing importance of water reuse and the discussion on enhanced treatment of wastewaters for micropollutant removal may



igure . The Mülheim process with the characteristic combination of ozonation and biological filtration. With permission of RWW Rheinisch-Westfälische Wasserwerksgesellschaft mbH.

As mentioned above, the implementation of the Mülheim process in 1974 was a considerable break-through in chlorine-free drinking water treatment. In a first step, the water passes through a slow sand filter. Thereby, suspended particles are retained and part of the organic matter is consumed by microbial processes. Subsequent ozonation oxidises micropollutants and transforms part of the remaining DOM to AOC/BDOC (Chapter 3), which leads to a further reduction of DOC in the following biofiltration step with multi-layer filters containing activated carbon (AC). The water is then UV-disinfected prior to distribution. In case of emergency, chlorine or chlorine dioxide dosing is possible.

Since the 1990s, membrane filtration, in particular UF, has become an interesting alternative to deep bed sand filtration processes. UF is an efficient barrier against micro-organisms (viruses, bacteria and protozoa) but does not retain organic micropollutants (Jacangelo et al., 1997). Therefore, a combination of UF with ozone oxidation and adsorption processes leads to a drinking water with good hygienic and chemical qualities.

Figure 5.3 shows a conventional process combination including ozonation and deep bed filtration processes and two possible process combinations including UF, ozonation and AC filtration (Pronk & Kaiser, 2008).

All three process combinations are currently used for the treatment of Lake Zurich water in Switzerland. Combination C may require a final disinfection with UV, because AC filters lose significant numbers of micro-organisms. In a pilot study with combination B, the total cell count determined by flow cytometry was 10<sup>3</sup> cells/mL after ozonation and . 10<sup>5</sup> cells/mL after AC filtration (cf. Figure 5.4) (Hammes et al., 2008).

In the AC filter, bacteria can grow on AOC/BDOC, which leads to a significant increase in the total cell count (Figure 5.4). In combination B which is reflected in Figure 5.4, bacteria are removed by UF to below detection limit of flow cytometry, whereas in combination C, where AC filtration is the last treatment step, they would be released into the distribution system if not properly disinfected.

Integration of ozonation in drinking water and wastewater process trains

igure . Assimilable organic carbon (AOC) formation and total cell counts (TCC, determined by flow cytometry) for ozonation followed by biological sand filtration for a full-scale wastewater treatment plant, Regensdorf, Switzerland (25000 population equivalent). Ozone dose 1.24 g  $O_3/g$  DOC. In: Secondary effluent, inlet to ozone reactor; P1, P3, P7 sampling points within the reactor; SF sand filtration. Adapted from Zimmermann **et al.**, 2011, with permission.

Energy requirements for micropollutant transformations during ozonation and advanced oxidation processes (AOPs) depend on the matrix of the water that consumes oxidants (Chapter 3, mainly type and concentration of DOM) and the rate constant for the reaction of a target compound with ozone and <sup>†</sup>OH radicals. Table 5.4 shows a comparison of the energy requirements for a 90% transformation of selected compounds during ozonation and the AOP UV/H<sub>2</sub>O<sub>2</sub> for laboratory experiments. In general, an increase in energy of about 25% for O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> relative to the conventional ozonation is estimated based on production energy of 15 kWh/kg and 10 kWh/kg for ozone and H<sub>2</sub>O<sub>2</sub>, respectively (Katsoyiannis et al., 2011). For ozonation, Table 5.4 shows that for a given water quality, the required energy increases in the order SMX, pCBA, ATR, NDMA. This can be explained by a decrease in the second order rate constants for the reaction of these compounds with ozone and <sup>†</sup>OH from SMX to NDMA. Energy requirements also increase significantly from Lake Zurich water to Dübendorf wastewater, due to the higher concentrations of DOM (consumption of ozone and <sup>†</sup>OH, Chapter 3) and carbonate (consumption of <sup>†</sup>OH, Chapter 3). For a given water, energy requirements for UV/H<sub>2</sub>O<sub>2</sub> are typically significantly higher and depend on the penetration depth of UV radiation. Only for NDMA, with low reactivity towards ozone and <sup>†</sup>OH (Lee et al., 2007b), does the energy requirement for UV/H<sub>2</sub>O<sub>2</sub> become comparable to ozonation. This is due to the fact that NDMA undergoes mainly direct photolysis (Sharpless & Linden, 2003).

For a particular full-scale study (Hollender et al., 2009), the energy consumption for ozonation of secondary effluent, including all contributions (production of liquid oxygen, its transport, generation of ozone) was calculated. The energy requirement at the plant remained constant for process gas in the range of 100 170 g  $O_3$  m  $^3$  at 12 kWh/kg  $O_3$ . This translates into an energy requirement of 0.035 kWh m  $^3$  for a specific ozone dose of 0.6 g  $O_3$ /g DOC, which corresponds to about 12% of the total energy consumption of a nutrient (C, N, P) removal plant (0.3 kWh m  $^3$ ). In addition,

production of pure oxygen requires 0.01 0.015 kWh m  $^3$ . Therefore, the overall energy requirement at this ozone dose (removal of SMX) is quite similar to that shown in Table 5.4 for laboratory systems. For a large range of wastewaters (10,000 to 500,000 person equivalents) and DOC contents (6 to 20 g DOC m  $^3$ ), total costs of ozonation (investment and operation including post-filtration step) were estimated to range between 0.05 and 0.15  $\in$  m  $^3$ , depending on plant size and secondary effluent quality (Joss et al., 2008).

Table . Energy requirements in kWh m  $^3$  for 90% transformation of selected micropollutants by conventional ozonation in Lake Zurich water and Dübendorf wastewater and by using UV(254 nm)/  $H_2O_2$  (0.2 mM) for varying optical path lengths (cm) in Lake Zurich water. Experimental conditions: target compound concentration  $0.5~\mu\text{M}$ , pH 8, **T**  $20~^\circ\text{C}$ . According to Katsoyiannis **et al** , (2011), with permission

	ake urich ater	bendorf wastewater	ake urich ater		
Target compound	onation	onation	U /	U / cm	U / cm
SMX	0.0015	0.045	0.39	0.15	0.11
рСВА	0.035	0.2	0.75	0.23	0.17
ATR	0.05	0.3	0.98	0.28	0.2
NDMA	0.5	0.9	1.62	0.44	0.3

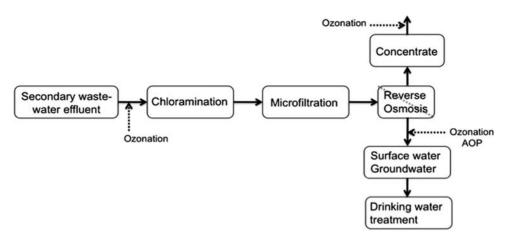
SMX sulfamethoxazole; pCBA -chlorobenzoic acid; ATR atrazine; NDMA -nitrosodimethylamine; Lake Zurich water, DOC 1.3 mgC/L, carbonate alkalinity 2.6 mM; Dübendorf wastewater, DOC 3.9 mg C/L, carbonate alkalinity 6.5 mM.

#### . S U E T

The removal of micropollutants from the wastewater stream by enhanced treatment of secondary wastewater effluent is an end-of-pipe solution. Other options include treatment of source-separated urine (Larsen & Gujer, 1996) or treatment of other point sources such as hospital wastewater. Urine separation and treatment with ozone has been demonstrated to be a feasible process for micropollutant removal. Even though it only accounts for about 1% of the wastewater stream, it requires more energy to remove micropollutants by ozonation than in wastewater (Dodd et al., 2008). When the treatment of source-separated urine is combined with nutrient recovery (N, P), the overall energy requirement becomes even favourable for urine treatment compared to wastewater treatment (Dodd et al., 2008). Nevertheless it has to be considered that some chemicals, among them high risk chemicals such as the antiarrhythmic compound amiodarone (cf. Chapter 8), are excreted via faeces (Escher et al., 2011). Therefore, the full spectrum of compounds will not be removed by this approach. The contribution of hospital wastewater to the overall load of pharmaceuticals in municipal wastewater is typically quite low in the order of , 15% (Ort et al., 2010). Nevertheless, source control in hospitals has guite high acceptance among stakeholders, especially if the contribution of hospitals to the overall load is high (Lienert et al., 2011). In this context it is noted that municipal wastewater receives an integrated load of chemicals used in households, which also include biocides, pesticides, personal care products, etc., which will also be removed by an ozone treatment of secondary effluents (Hollender et al., 2009).

#### F M T STF TF

Reclamation of wastewater as a resource for drinking water and for irrigation purposes (agriculture, golf courses, etc.) has become an important issue in arid and semi-arid areas due to population growth and climate change. Today, wastewater reuse is heavily based on membrane processes. Secondary effluent is typically treated by a combination of microfiltration/ultrafiltration with reverse osmosis (RO) (Figure 5.7) (Asano et al., 2007). Even in coastal areas this approach (, 1 kWh/m<sup>3</sup>) is more energy efficient than seawater desalination [3.5 4.5 kWh/m<sup>3</sup>, (Sommariva, 2010)]. Water desalination has become increasingly important worldwide with large-scale plants (30,000 320,000 m<sup>3</sup>/d) in Kuwait, Singapore, USA, Australia and China (Hemmi et al., 2010). The RO process is frequently followed by UV disinfection, and the water is then mostly used for replenishment of natural water bodies such as groundwaters or surface waters. In the treatment scheme outlined in Figure 5.7, ozonation is not applied. In principal, ozonation could be used to treat secondary wastewater effluent for removing NDMA precursors (Lee et al., 2007a). Such (unknown) precursors may lead to NDMA during chloramination which is routinely applied to hinder biofilm growth on the RO membrane. Typically, the rejection of micropollutants by RO is . 90% (Busetti et al., 2009). Advanced oxidation of the RO permeate (UV/H<sub>2</sub>O<sub>2</sub>, UV/ozone or ozone/H<sub>2</sub>O<sub>2</sub> is an option for an additional barrier for removing micropollutants such as NDMA, which are not fully retained by RO. AOPs in post-RO water are expected to be very efficient, because its <sup>†</sup>OH scavenging rate is very low due to its low DOC of, 0.1 mg/L.

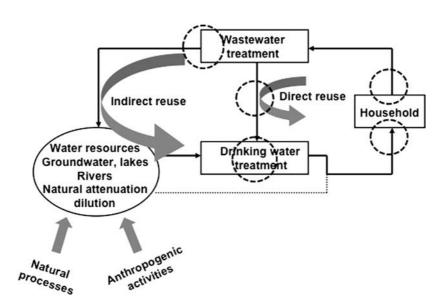


igure . Water reuse scheme based on ultrafiltration/reverse osmosis. Points for potential ozonation steps are also indicated.

One of the problems in the RO-based water reuse scheme is the discharge of the RO concentrate. The concentration factor for micropollutants during RO treatment of wastewater is of the order of four. In a recent study, ozonation was investigated for the elimination of beta blockers from an RO concentrate with a DOC of 46 mg/L (Benner et al., 2008). For metoprolol (cf. Chapter 8) [k(O<sub>3</sub>)  $2 \times 10^3$  M  $^1$ s  $^1$  (pH 7), k( $^1$ OH)  $^1$ OH)  $^1$ OH  $^$ 

Integration of ozonation in drinking water and wastewater process trains

Based on the discussion above, potential points of application of ozonation processes for micropollutant abatement in the urban water cycle are shown in Figure 5.9.



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In principle, ozonation can be applied in households as point-of-entry or point-of-use treatment and to the wastewater, e.g. source separated urine (Dodd et al., 2008). Once the wastewater is collected, oxidative treatment may be carried out as post-treatment of secondary wastewater effluent (see above). Compared to treatment of source-separated urine, this also allows oxidative transformation of micropollutants which are derived from sources other than households. Both the treatment at the household level and the treatment in centralised wastewater treatment plants lead to a reduction of the micropollutant discharge to the receiving water bodies. As a consequence, ecosystems and water resources are protected from adverse impacts. When the urban water system is mainly driven by human toxicology, oxidative treatment (mainly ozonation or AOPs) may be placed within the drinking water treatment scheme (Westerhoff et al., 2005; Broséus et al., 2009; Vieno et al., 2007; Kruithof et al., 2007; Ternes et al., 2002).

This scenario has the advantage that micropollutants from diffuse sources such as agriculture, traffic and natural sources (e.g. cyanotoxins and taste and odour compounds) will also be removed (Acero et al., 2000, 2001; Benitez et al., 2007; Rodriguez et al., 2007; Peter & von Gunten, 2007; Onstad et al., 2007). For direct or indirect potable water reuse, an oxidation can be applied after a reverse osmosis treatment (Asano et al., 2007). The water quality for each treatment scenario is decisive for the efficiency of an ozonation process. The main parameter is the content of the dissolved organic matter, typically expressed as DOC concentration (Chapter 3). In addition, pH, alkalinity and ammonia also play an important role (Chapter 3). Table 5.5 summarises water qualities of hydrolysed and electrodialysed urine, municipal wastewater and water resources used for drinking water production.

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Electrodialysed urine diluate*	8	400*	30	400
Wastewater effluent	7 8	5 20	2 4	20
	ater resources fo	or drinking water	production	
Surface water	7 8	1 20	1 2	, 0.005 to . 1
Groundwater	7 8	, 1 to 20	1 5	, 0.005 to . 1

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A dramatic decrease of DOC is observed from hydrolysed urine to wastewater effluent. This is partially caused by dilution and partially by the DOC removal during activated sludge treatment. The DOC concentration in surface and groundwaters is typically much smaller and dominated by natural processes (soil weathering, algal growth, etc.). Because ozone demand is closely related to the DOM concentration, it is evident that ozone consumption gets smaller further away from the household source. However, it has to be taken into account, that human urine represents , 1% of the total flow of municipal wastewater. Therefore, it might still be a feasible option for micropollutant elimination.

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Table . Required ozone doses (mg/L) and corresponding O<sub>3</sub>/DOC ratios (w/w) for a 90% elimination of -ethinyloestradiol (EE2) and ibuprofen (IP) in various water sources (Lee & von Gunten, 2010; Dodd **etal**., 2008; Huber **et al**., 2003, 2005)

ater type	EE		Р	
	dose mg/	/ w/w	dose mg/	/ w/w
Hydrolysed urine	500	0.25	1000	0.5
Electrodialysed urine diluate*	150	0.375	600	1.5
Wastewater 1 (7.7 mg/L DOC)	. 1	. 0.13	n.d.	n.d.
Wastewater 2 (5 mg/L DOC)	0.5	0.1	4	0.8
Lake water (3.7 mg/L DOC)	0.1	0.03	n.d.	n.d.
River water (1.3 mg/L DOC)	, 0.1	, 0.08	. 2	. 2

n.d.: not determined;

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Table . Compilation of rate constant of ozone with olefins. Published rate constants rounded to significant figures (  ${\bf ntn}\ {\bf e}$  )

ompound	$pK_a$	р	k/M s	eference
Carbamazepine			$3 \times 10^5$	Huber <b>et al</b> , 2003
Cephalexin		7	$8.7 \times 10^4$	Dodd <b>et al</b> , 2010
Chlordane			, 0.04	Yao & Haag, 1991
5-Chlorouracil	8.0		$4.3 \times 10^3$	Theruvathu et al , 2001
anion			$1.3 \times 10^6$	Theruvathu et al , 2001
Cinnamic acid			$5 \times 10^{4}$	Leitzke <b>et al</b> , 2001
anion			$1 \times 10^5$ $3.8 \times 10^5$ $1.2 \times 10^6$	Jans, 1996 Leitzke <b>et al</b> , 2001 Jans, 1996
-Cyclocitral			$3.9 \times 10^3$	Peter & von Gunten, 2007
Cylindrospermopsin			$2.5 \times 10^6$	Onstad <b>et al</b> , 2007
Cytidine	4.15		$3.5 \times 10^3$	Theruvathu <b>et al</b> , 2001
protonated			40	Theruvathu <b>et al</b> , 2001
Cytosine	4.6, 12.2		1.4 <b>x</b> 10 <sup>3</sup> 930	Theruvathu <b>et al</b> , 2001 Ishizaki <b>et al</b> , 1984
protonated anion			18 1.5 <b>x</b> 10 <sup>6</sup>	Theruvathu <b>et al</b> , 2001 Theruvathu <b>et al</b> , 2001 Ishizaki <b>et al</b> , 1984
2 -Deoxyadenosine protonated	3.8		14 5	Theruvathu <b>et al</b> , 2001 Theruvathu <b>et al</b> , 2001
2 -Deoxycytidine protonated	4.3		3.5 <b>x</b> 10 <sup>3</sup>	Theruvathu <b>et al</b> , 2001 Theruvathu <b>et al</b> , 2001
5 -Deoxycytidylic acid	4.6		$1.4 \times 10^3$	Ishizaki <b>et al</b> , 1984
2 -Deoxyguanosine	2.5, 9.2		$1.9 \times 10^4$	Theruvathu <b>et al</b> , 2001
5 -Deoxyguanylic acid	2.9, 9.7		$4 \times 10^4$	Ishizaki <b>et al</b> , 1984
1,1-Dichloroethene			110	Dowideit & von Sonntag, 1998
s-1,2-Dichloroethene			310 540	Yao & Haag, 1991 Dowideit & von Sonntag, 1998
trans 1,2-Dichloroethene			$6.5 \times 10^3$ $6.5 \times 10^3$	Dowideit & von Sonntag, 1998 Hoigné & Bader, 1983a
Dichloromaleic acid		3.3	10	Leitzke & von Sonntag, 2009
1,1-Dichloropropene			$2.6 \times 10^3$	Dowideit & von Sonntag, 1998
Diethyl vinylphosphonate			$3.3 \times 10^{3}$	Leitzke <b>et al</b> , 2003
3,4-Dihydroxycinnamic acid			$2 \times 10^6$	Jans, 1996
anion			$1.2 \times 10^7$	Jans, 1996
1,3-Dimethyluracil			$2.8 \times 10^{3}$	Theruvathu <b>et al</b> , 2001
DNA			410	Theruvathu <b>et al</b> , 2001
Endrin			, 0.02	Yao & Haag, 1991

( **ntn e** )

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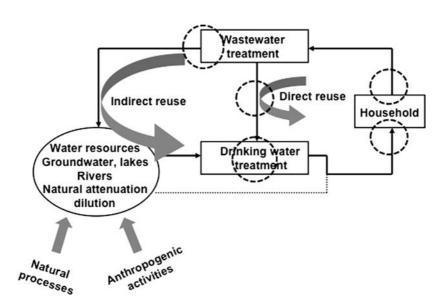
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Cytidine	4.15		3.5 <b>×</b> 10 <sup>3</sup> 40	Therwyathu <b>et al</b> , 2001
protonated Cytosine	4.6, 12.2		1.4 × 10 <sup>3</sup>	Theruvathu <b>et al</b> , 2001 Theruvathu <b>et al</b> , 2001
Cytosine	4.0, 12.2		930	Ishizaki <b>etal</b> ., 1984
protonated			18	Theruvathu <b>et al</b> , 2001
anion			$1.5 \times 10^6$	Theruvathu <b>et al</b> , 2001
				Ishizaki <b>et al</b> , 1984
2 -Deoxyadenosine	3.8		14	Theruvathu <b>et al</b> , 2001
protonated			5	Theruvathu <b>et al</b> , 2001
2 -Deoxycytidine	4.3		$3.5 \times 10^3$	Theruvathu <b>et al</b> , 2001
protonated			44	Theruvathu <b>et al</b> , 2001
5 -Deoxycytidylic acid	4.6		$1.4 \times 10^3$	Ishizaki <b>et al</b> , 1984
2 -Deoxyguanosine	2.5, 9.2		$1.9 \times 10^4$	Theruvathu <b>et al</b> , 2001
5 -Deoxyguanylic acid	2.9, 9.7		4 × 10 <sup>4</sup>	Ishizaki <b>et al</b> , 1984
1,1-Dichloroethene			110	Dowideit & von Sonntag, 1998
s-1,2-Dichloroethene			310	Yao & Haag, 1991
			540	Dowideit & von Sonntag, 1998
trans 1,2-Dichloroethene			$6.5 \times 10^{3}$	Dowideit & von Sonntag, 1998
			$6.5 \times 10^3$	Hoigné & Bader, 1983a
Dichloromaleic acid		3.3	10	Leitzke & von Sonntag, 2009
1,1-Dichloropropene			$2.6 \times 10^3$	Dowideit & von Sonntag, 1998
Diethyl vinylphosphonate			$3.3 \times 10^{3}$	Leitzke <b>et al</b> , 2003
3,4-Dihydroxycinnamic acid			$2 \times 10^6$	Jans, 1996
anion			$1.2 \times 10^7$	Jans, 1996
1,3-Dimethyluracil			$2.8 \times 10^{3}$	Theruvathu <b>et al</b> , 2001
DNA			410	Theruvathu <b>et al</b> , 2001
Endrin			, 0.02	Yao & Haag, 1991

( ntn e )

Table . Compilation of rate constant of ozone with olefins. Published rate constants rounded to significant figures ( **ntn e** )

ompound	$pK_a$	р	k/M s	eference
Oseltamivir acid		7 8	1.7 × 10 <sup>5</sup>	Mestankova <b>et al</b> , 2012
1-Penten-3-one			$5.9 \times 10^4$	Peter & von Gunten, 2007
Progesterone			480	Barron et al , 2006
Propene			8 × 10 <sup>5</sup>	Dowideit & von Sonntag, 1998
Sorbic acid anion	4.76	3 8	$3.2 \times 10^5$ $9.6 \times 10^5$	Onstad <b>et al</b> , 2007
Tetrachloroethene			, 0.1	Hoigné & Bader, 1983a
Tetramethylethene			. 1 <b>x</b> 10 <sup>6</sup>	Dowideit & von Sonntag, 1998
Thymidine anion	9.8		$3 \times 10^4$ $1.2 \times 10^6$	Theruvathu <b>et al</b> , 2001 Theruvathu <b>et al</b> , 2001
5 -Thymidylic acid	10.0		$1.6 \times 10^4$	Ishizaki <b>et al</b> , 1984
Thymine anion	9.9		$4.2 \times 10^4$ $2.3 \times 10^4$ $3 \times 10^6$	Theruvathu <b>et al</b> , 2001 Ishizaki <b>et al</b> , 1984 Theruvathu <b>et al</b> , 2001
Trichloroethene			17 15 14	Hoigné & Bader, 1983a Yao & Haag, 1991 Dowideit & von Sonntag, 1998
Tylosin protonated	7.7		$7.7 \times 10^4$	Dodd <b>et al</b> , 2006a
Uracil anion	9.5		650 9.2 <b>x</b> 10 <sup>5</sup>	Theruvathu <b>et al</b> , 2001 Theruvathu <b>et al</b> , 2001
Vinyl acetate			$1.6 \times 10^5$	Leitzke <b>et al</b> , 2003
Vinyl bromide			$1 \times 10^4$	Leitzke <b>et al</b> , 2003
Vinyl chloride			$1.4 \times 10^4$	Dowideit & von Sonntag, 1998
Vinylene carbonate			$2.6 \times 10^4$	Leitzke <b>et al</b> , 2003
Vinyl phenyl sulfonate			200	Leitzke <b>et al</b> , 2003
Vinyl phosphonic acid monoanion dianion			$1 \times 10^4$ $2.7 \times 10^4$ $1 \times 10^5$	Leitzke <b>et al</b> , 2003 Leitzke <b>et al</b> , 2003 Leitzke <b>et al</b> , 2003
Vinyl sulfonate ion			$8 \times 10^{3}$	Leitzke <b>et al</b> , 2003

# . T E E EE ME SM

The 1,3-cyloadduct of ozone to olefins was named by Carl Friedrich Harries ozonide (Chapter 1). Mechanistic details were only later unravelled by Rudolf Criegee (Chapter 1), and the reaction of ozone with olefins bears his name. In water, olefins react essentially according to the Criegee mechanism [reactions (1) (9)], originally studied in organic solvents (Criegee, 1975). In water, however, ionic intermediates are intercepted [reaction (7)], and the reaction sequence, that in organic solvents proceeds to the Criegee ozonide, is arrested at an early stage (Dowideit & von Sonntag, 1998). As here ozone reactions in aqueous solution are discussed, the Criegee ozonide [cf. reaction (9)] can be disregarded, and whenever an ozonide is mentioned, the first ozonide is referred to.

Table . Products and their yields [with respect to ozone consumption (mol/mol)] in the ozonolysis of ethene and some of its methyl- and chlorine-substituted derivatives in aqueous solution according to Dowideit & von Sonntag (1998). Empty fields indicate that a given product is not expected to be formed and has not been looked for

Product	Ethene	Propene	Me	l Eu	, l	, l	l =	, l
			Ethene	Ethene	Ethene	Ethene	Ethene	Propene
HCI				1.05	1.95	2.02	2.87	2.05
HC(O)OH				0.06	0.03	1.01	0.82	
HC(O)OOH				0.02 <sup>(a)</sup>		0.98 <sup>(a)</sup>	0.88 <sup>(a)</sup>	
HOCH <sub>2</sub> COOH					0.07 <sup>(c)</sup>			
CO				1.01		1.08	0.04	
$CO_2$					0.90	0.02	0.95	1.01
CH <sub>2</sub> O	2.04	1.03			0.96			
CH <sub>3</sub> C(O)H		0.97						1.03
(CH <sub>3</sub> ) <sub>2</sub> CO			1.74					
HOCH <sub>2</sub> OOH	1.08 <sup>(b)</sup>			1.06 <sup>(b)</sup>	0.96 <sup>(b)</sup>			
CH₃CH(OH)OOH		0.99 <sup>(b)</sup>						0.98 <sup>(b)</sup>
(CH <sub>3</sub> ) <sub>2</sub> C(OH)OOH			(d)					
Cl <sub>2</sub> CHC(O)H					, 0.01 <sup>(c)</sup>			
CICH <sub>2</sub> C(O)OH					0.08 <sup>(c)</sup>			
Cl <sub>2</sub> CHC(O)OH							0.04 <sup>(c)</sup>	
$[(CH_3)_2C(OH)]_2$			0.1					

<sup>(</sup>a) Precursor of formic acid. (b) Precursor of aldehydes. (c) Product of partial oxidation reaction. (d) The reaction with molybdate-activated iodide is too slow for its determination.

Its good solubility in water and its high rate constant (Table 6.1) makes buten-3-ol a very convenient competitor for the determination of ozone rate constants (Chapter 2).

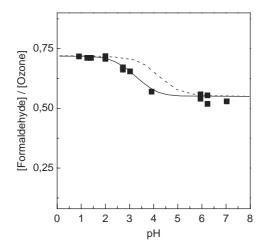
With halogenated olefins, reactive halogen-containing intermediates are formed which show an interesting chemistry. With vinyl chloride the main reaction path leads to hydroxymethylhydroperoxide and formyl chloride [reaction (15)]. Formyl chloride rapidly decomposes into CO and HCI [reaction (19), k  $600 \, \text{s}^{-1}$ ; 94%] (Dowideit et al., 1996). Its hydrolysis into formic acid plus HCI [reaction (18), 6%] is slow in comparison but gains in importance at high pH [reaction (17), k(OH )  $2.5 \times 10^4$  M  $^{-1} \, \text{s}^{-1}$ ]. A minor route leads to chlorohydroxymethylhydroperoxide [reaction (16)]. The geminal chlorohydrine substructure in chlorohydroxymethylhydroperoxide is very unstable and rapidly loses HCI [on a low microsecond timescale (Köster & Asmus, 1971; Mertens et al., 1994)] giving rise to formic peracid [reaction (20)]. Formic peracid is generated in the reaction of 1,2-dichloroethene (see below), and this is a convenient method for its formation [for its reactions see (Flyunt et al., 2003a)].

Formyl bromide, the product of the analogous reaction of vinyl bromide with ozone also decomposes preferentially into CO plus HBr. With 3.6%, the formic acid yield is lower than the corresponding yield from formyl chloride (6%). Whether this is due to a faster decomposition or a slower hydrolysis is not yet known.

1,2-Dichloroethene is symmetrical, and the primary products are chlorohydroxymethylhydroperoxide and formyl chloride [reactions (32) and (33)]. HCl, CO and formic peracid are the main final products (see above).

Moreover, cleavage along the O O and C C bonds of the envisaged dioxetane intermediate [cf. reaction (57)] does not take place.

Depending on the protonation state of the carboxylic group, there is some bias in the branching between reactions (55) and (56). As expected, the deprotonated carboxyl group decarboxylates more readily favouring reaction (56). Formaldehyde, which is produced from reaction (55), can be measured with some accuracy. A plot of the formaldehyde yield as a function of pH is shown in Figure 6.3.



igure . The pH dependence of the formaldehyde yield in the ozonolysis of acrylic acid. The dashed line indicates how this dependence would look if it were governed by the  $p_a$  value of acrylic acid. From Leitzke & von Sonntag, 2009 with permission.

The inflection point is at pH 3, markedly distant from the p $K_a$  value of acrylic acid, 4.25 (dashed line). It may reflect the p $K_a$  value of the ozonide, as the zwitterion is most likely not an intermediate, but if it were it would be too short-lived for the p $K_a$  equilibrium to become established during its lifetime.

The reactions of methacrylic acid ozonide are depicted in reactions (63) (67).

#### **Olefins**

indication that the hydrogen at N1 must be involved. Singlet oxygen formation is much more prominent (45%) with 5-chlorouracil (Table 6.7). For this nucleobase derivative some preliminary data are available (Muñoz et al., 2001) and shed some light on the mechanism. The hydrogen at N1 in the ozonide is most likely acidic [equilibrium (103)].

Subsequent cleavage of the ozonide yielding an isopyrimidine hydrotrioxide [reaction (104)] will be followed by the release of  ${}^{1}O_{2}$  [reaction (105); for a compilation of  ${}^{1}O_{2}$  yields in nucleic acid constituents see Table 6.7], CI release [reaction (106)] and water addition [reaction (107); for the formation and reactions of isopyrimidines see Al-Sheikhly et al. (1984); Schuchmann et al. (1984)]. At high pH isodialuric acid and HCl are indeed major products.

Table . Singlet oxygen yields (in % of mol  $O_3$  consumed) in the reaction of ozone with nucleic acid constituents (Muñoz **et al**, 2001)

Substrate	p	yield	Molar ratio
			substrate:o one
Uracil (Ura)	3.5	No signal	9:1
	7	6	9:1
	11	7	9:1
1,3-Dimethyluracil	3.5	No signal	4:1
	11	No signal	4:1
6-Methyluracil	3.5	No signal	10:1
	7	12	10:1
	10	15	10:1
5-Chlorouracil	3.5	No signal	4:1
	7	45	4:1
	11	43	4:1
Thymine (Thy)	3.5	No signal	4:1
	7	4	4:1
	10	8	4:1
Thymidine (Thyd)	7	No signal	10:1
, ,	10	No signal	4:1

(ntne)

The -lactam cephalosporin antibiotic cephalexin has two ozone-reactive sites, the sulfide function and a C C double bond. Both contribute to its ozone-induced degradation. Details are discussed in Chapter 9. The sulfoxides that are formed upon the reaction of ozone continue to react readily with ozone at the C C double bond, while the sulfoxide function is only of little reactivity (Chapter 9). The reaction of ozone with the cephalexin (R)-sulfoxide to the corresponding Criegee product [reaction (112)] takes place to only 30% (Dodd, 2008, 2010).

Based on the reactions of acrylic and methacrylic acids discussed above, one would expect that a decarboxylation reaction should occur in competition. The product of this reaction has not yet been identified.

Tylosin, a macrolide antibiotic, has conjugated double bonds and a tertiary amine. The reactivity of the two conjugated C C double bonds in conjugation with a carbonyl function must be an order of magnitude higher than a single C C double bond in conjugation with a carbonyl group, as in progesterone, if a comparison of muconic acid with fumaric acid is a good guide (Table 6.1). The reactivity in the pH range relevant for water treatment is mostly controlled by the tertiary amine group (Dodd et al., 2006) and will therefore be discussed in Chapter 8, where the formula of tylosin is also shown.

Tetracycline, another antibiotic compound has multiple sites for ozone attack, namely two olefins, a phenolic group and a tertiary amine. In the pH range relevant for water treatment, tetracycline will preferentially react with the phenolic moiety (Dodd et al., 2006a) and will therefore be discussed in Chapter 7, where the formula of tetracycline is also given.

The antiviral drugs stavudine, zidovudine and lamivudine are thymine derivatives. They have been detected in WWTPs (Prasse et al., 2010).

They should be readily eliminated upon ozonation (cf. the rate constant of thymidine in Table 6.1). Stavudine and lamivudine have additional sites for ozone attack, a further C C double bond and a sulfur, respectively.

The antiviral drugs aciclovir (acyclovir) and penciclovir, also detected in wastewater, belong to the guanine family and with aciclovir ozone rate constants follow closely those of guanine derivatives (Table 6.1). Product formation is due to ozone attack at the C(4) C(5) double bond (Prasse et al., 2012).

#### **Olefins**

peptidic ring system, it is responsible for the hepatoxicity of the microcystins. The reaction of ozone with the conjugated double bonds of the ADDA group is fast (Table 6.1). It leads to a cleavage of the ADDA group and hence to a loss of toxicity. In the oxidation of MC-LR by permanganate, the degradation of the parent compound also leads to a loss of its toxicity (Rodríguez et al., 2008). Similar to ozone, it can be assumed from the reactivity of permanganate with olefins that the main site of attack for permanganate is the ADDA group (Waldemer & Tratnyek, 2006; Hu et al., 2009).

Microcystine-LR

Cylindrospermopsin, another cyanotoxin, contains a uracil derivative, which is the active moiety that inhibits protein translation to promote hepatoxicity or binds to DNA causing strand breakage and genotoxicity (Banker et al., 2001). The main site of attack is the uracil double bond (Onstad et al., 2007), and its ozone chemistry will be similar to that of thymine/thymidine discussed above. Most importantly, the uracil group will be altered significantly which should lead to a loss of the toxic properties of cylindrospermopsin.

$$\begin{array}{c} O \\ O = S - O^- \\ O \end{array}$$

Cylindrospermopsin

Anatoxin-a is also a cyanotoxin which mimics acetylcholine and over-stimulates muscle cells and may cause paralysis (Carmichael et al., 1979).

Anatoxin-a

Anatoxin has two functional groups, the amino group and an olefinic function. The reactivity  $pK_a$  of anatoxin-a is 7.88, which means that the olefinic group dominates the reactivity (Table 6.1) for most of

the drinking water relevant pH range (Onstad et al., 2007). The opening of the aliphatic ring caused by a Criegee-type reaction will most likely lead to a loss of anatoxin-a s toxicity.

The mycotoxin patulin is often found in apple juice, and its destruction by ozone has been suggested (Cataldo, 2008). Ozone rate constant and reaction products are as yet not known. The rate constant must be considerably lower than that of -ionone (Table 6.1), as the carbonyl group in conjugation with the two C C double bonds withdraws electron density from the sites of ozone attack.

Another class of natural olefin-containing compounds consists of algae derived taste and odour compounds, such as -ionone, -cyclocitral, 1-penten-3-one, cis-3-hexen-1-ol and trans,cis-2,6-nonadienal (for rate constants see Table 6.1; for an overview of taste and odour compounds and their properties see Chapter 5).

H<sub>3</sub>C CH<sub>3</sub> 
$$H_3$$
C CH<sub>3</sub>  $H_2$ C CH<sub>3</sub>  $H_2$ C CH<sub>3</sub>  $H_3$ C CH<sub>3</sub>  $H_4$ C CH<sub>4</sub>  $H_4$ 

These compounds will react with a Criegee-type reaction, leading to more hydrophilic compounds (Peter & von Gunten, 2007). Since evaporation of these compounds is an important property for their transfer into the cavity of the nose where the odour receptors are, oxidation by ozone is an efficient way to mitigate taste and odour problems caused by olefinic compounds in drinking waters.

The hormones progesterone and testosterone also contain an olefinic group. Progesterone reacts very moderately with ozone (Table 6.1), because of the electron-withdrawing effect of the carbonyl group in conjugation. The reactivity of testosterone is expected to be the same.

The reaction of ozone leads to a rupture of the 6-membered ring (Barron et al., 2006). This must significantly reduce the biological activity of progesterone and testosterone. Product formation has been studied for progesterone and is shown in reactions (113) (115) (Barron et al., 2006).

The ozonide (not shown) cleaves the ring leading to aldehyde and hydroxyhydroperoxide functions. The  $H_2O_2$  elimination [reaction (113)] is trivial and predominates under the given conditions, but a minor pathway leads to a (well-established) addition of the hydroperoxide to the carbonyl group [equilibrium (114)]. This adduct decomposes after deprotonation of the acidified hydroxyl group [reaction (115)].

The herbicides endrin and chlordane are particularly unreactive towards ozone with respect to its parent cis-1,2-dichloroethene (Table 6.1).

This low reactivity has been suggested to be due to a steric hindrance of the C C double bond on both sides (Yao & Haag, 1991).

# Chapter 7

# Aromatic compounds

. E T T M T MP U S

The rate constants of ozone with aromatic compounds vary strongly with the nature of substituents, with ten orders of magnitude between nitrobenzene and phenolate ion (Table 7.1).

Table . Compilation of rate constants for the reaction of ozone with aromatic compounds. For nitrogen heterocyclic aromatic compounds and aromatic compounds with nitrogen-containing groups in the side chain see Chapter 8. Published rate constants are rounded to significant figures

ompound	p <b>K</b> a	р	k/M s	eference
Amidotrizoic acid			, 0.8	Huber <b>et al</b> , 2003
			0.05	Real <b>et al</b> ., 2009
Benzaldehyde			2.5	Hoigné & Bader, 1983b
Benzene			2	Hoigné & Bader, 1983a
Benzenesulfonate			0.23	Yao & Haag, 1991
Benzoate ion			1.2	Hoigné & Bader, 1983b
Bezafibrate			590	Huber <b>et al</b> , 2003
Bisphenol A	9.6, 10.2		$1.7 \times 10^4$	Deborde <b>et al</b> , 2005
mono-anion			$1.1 \times 10^9$	Deborde <b>et al</b> , 2005
di-anion			$1.1 \times 10^9$	Deborde <b>et al</b> , 2005
Carbofuran			640	Yao & Haag, 1991
Catechol		7	5.2 <b>x</b> 10 <sup>5</sup>	Mvula & von Sonntag, 2003
			$3.1 \times 10^5$	Gurol & Nekouinaini, 1984
Chlorobenzene			0.75	Hoigné & Bader, 1983a
2-Chlorophenol	8.3		1100	Hoigné & Bader, 1983b
anion			$2 \times 10^{8}$	Hoigné & Bader, 1983b
4-Chlorophenol	9.2		600	Hoigné & Bader, 1983b
anion			6 <b>x</b> 10 <sup>8</sup>	Hoigné & Bader, 1983b

( ntn e )

Table . Compilation of rate constants for the reaction of ozone with aromatic compounds. For nitrogen heterocyclic aromatic compounds and aromatic compounds with nitrogen-containing groups in the side chain see Chapter 8. Published rate constants are rounded to significant figures ( **ntn e** )

ompound	$pK_{a}$	р	k/M s	eference
2-(4-Chlorophenoxy)-2-			, 20	Huber <b>et al</b> , 2005
methylpropionic				
acid (Clofibric acid)			4	
2-Cresol			$1.2 \times 10^4$	Hoigné & Bader, 1983b
3-Cresol			$1.3 \times 10^4$	Hoigné & Bader, 1983b
4-Cresol			$3 \times 10^4$	Hoigné & Bader, 1983b
1,3-Dichlorobenzene			0.57	Yao & Haag, 1991
1,4-Dichlorobenzene			3	Hoigné & Bader, 1983b
2,3-Dichlorophenol	7.7		, 2000	Hoigné & Bader, 1983b
2,4-Dichlorophenol	7.8		, 1500	Hoigné & Bader, 1983b
anion			8 × 10 <sup>9</sup>	Hoigné & Bader, 1983b
2,4-Dichlorophenoxyacetic acid (2,4-D)		2	5.3	Xiong & Graham, 1992
Diethylphthalate			0.1	Yao & Haag, 1991
1,4-Dimethoxybenzene			$1.3 \times 10^5$	Muñoz & von Sonntag, 2000a
1,2-Dimethoxytoluene			$8.9 \times 10^4$	Ragnar <b>et al</b> , 1999a
2,3-Dimethylphenol			$2.47 \times 10^4$	Gurol & Nekouinaini, 1984
2,4-Dimethylphenol			$1.95 \times 10^4$	Gurol & Nekouinaini, 1984
2,6-Dimethylphenol			$9.88 \times 10^4$	Gurol & Nekouinaini, 1984
3,4-Dimethylphenol			$9.88 \times 10^4$	Gurol & Nekouinaini, 1984
Dimethylphthalate			0.2	Yao & Haag, 1991
2,6-Di- <b>t</b> -butyl-4-methylphenol (BHT)			$7.4 \times 10^4$	Peter & von Gunten, 2007
2,4-Dinitrotoluene		2	, 14	Chen <b>et al</b> , 2008
2,6-Dinitrotoluene		2	, 14	Chen <b>et al</b> , 2008
			5.7	Beltrán <b>et al</b> , 1998
17 -Ethinyloestradiol	10.4		$1.8 \times 10^5$	Deborde <b>et al</b> , 2005
anion			$3.7 \times 10^9$	Deborde <b>et al</b> , 2005
			$7 \times 10^9$	Huber <b>et al</b> , 2003
Ethylbenzene			14	Hoigné & Bader, 1983a
Galaxolide (HHCB)			140	Nöthe <b>et al</b> , 2007
Gemfibrozil			2 × 10 <sup>4</sup>	Estimated, see section 7.4
2,2,4,4,5,5-Hexachlorobiphenyl			, 0.9	Yao & Haag, 1991
Hydroquinone		2.6	$1.5 \times 10^6$	Gurol & Nekouinaini, 1984
-		7	$2.3 \times 10^6$	Mvula & von Sonntag, 2003
		3	$1.8 \times 10^6$	Mvula & von Sonntag, 2003

( ntn e )

## Aromatic compounds

Table . Compilation of rate constants for the reaction of ozone with aromatic compounds. For nitrogen heterocyclic aromatic compounds and aromatic compounds with nitrogen-containing groups in the side chain see Chapter 8. Published rate constants are rounded to significant figures ( **ntn e** )

ompound	$pK_{a}$	р	k/M s	eference
Ibuprofen [2-(4-Isobutylphenyl)propionic acid] deprotonated	4.9		7.2	Vel Leitner & Roshani, 2010
			9.6	Huber <b>et al</b> , 2003
Iomeprol			, 0.8	Huber <b>et al</b> , 2003
Iopamidol			, 0.8	Huber <b>et al</b> , 2003
Iopromide			, 0.8	Huber <b>et al</b> , 2003
Isopropylbenzene			11	Hoigné & Bader, 1983b
Methoxybenzene			290	Hoigné & Bader, 1983a
Methoxychlor			270*	Yao & Haag, 1991
4-Methoxy-1-naphthalenesulfonic acid		7	$3.6 \times 10^3$	Benner <b>et al</b> , 2008
Methylbenzoate			1.1	Hoigné & Bader, 1983b
2-Methyl-4-chlorophenoxyacetic acid (MCPA)		2	11.7	Xiong & Graham, 1992
2-Methyl-4- chlorophenoxypropionic acid (Mecoprop)		2	40	Beltrán <b>et al</b> , 1994
		7	111	Beltrán <b>et al</b> , 1994
		2	12.2	Xiong & Graham, 1992
1-Methylnaphthalene			$1 \times 10^{3}$	Legube <b>et al</b> , 1986
2-Methylphenol	10.2		$1.2 \times 10^4$	Hoigné & Bader, 1983b
3-Methylphenol	10.0		$1.3 \times 10^4$	Hoigné & Bader, 1983b
Naphthalene			3000	Hoigné & Bader, 1983a
			1500	Legube <b>et al</b> , 1986
Naproxen			$2 \times 10^{5}$	Huber <b>et al</b> , 2005
Nitrobenzene			9 × 10 <sup>2</sup>	Hoigné & Bader, 1983a
			2.2	Beltrán <b>et al</b> , 1998
4-Nitrophenol	7.2		, 50	Hoigné & Bader, 1983b
anion			$1.7 \times 10^7$	Hoigné & Bader, 1983b
4Nonylphenol	10.7		$3.8 \times 10^4$	Deborde <b>et al</b> , 2005
•			$3.9 \times 10^4$	Ning <b>et al</b> , 2007b
anion			6.8 × 10 <sup>9</sup>	Deborde <b>et al</b> , 2005
4-Octylphenol			$4.3 \times 10^4$	Ning <b>et al</b> , 2007b
17 -Oestradiol	10.4		$2.2 \times 10^5$	Deborde <b>et al</b> , 2005
anion			$3.7 \times 10^9$	Deborde et al , 2005
Oestriol	10.4		$1.0 \times 10^5$	Deborde et al , 2005
anion			$3.9 \times 10^9$	Deborde <b>et al</b> , 2005

( ntn e )

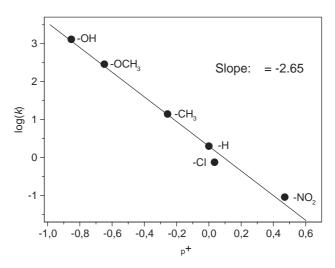
Table . Compilation of rate constants for the reaction of ozone with aromatic compounds. For nitrogen heterocyclic aromatic compounds and aromatic compounds with nitrogen-containing groups in the side chain see Chapter 8. Published rate constants are rounded to significant figures ( **ntn e** )

ompound	$pK_a$	р	k/M s	eference
Oestrone	10.4		$1.5 \times 10^5$	Deborde et al , 2005
anion			$4.2 \times 10^9$	Deborde <b>et al</b> , 2005
Paracetamol		2.0	$1.4 \times 10^3$	Andreozzi <b>et al</b> , 2003
		5.5	$1.3 \times 10^5$	Andreozzi <b>et al</b> , 2003
Pentabromophenol anion			$1.7 \times 10^6$	Mvula & von Sonntag, 2003
2,3,3 ,5,6-Pentachlorobiphenyl			, 0.05	Yao & Haag, 1991
Pentachlorophenol	4.7			
anion		2	$3 \times 10^{5}$	Hoigné & Bader, 1983b
			$1.2 \times 10^6$	Mvula & von Sonntag, 2003
Phenol	9.9		1300	Hoigné & Bader, 1983b
anion			$1.4 \times 10^9$	Hoigné & Bader, 1983b
1-Phenoxy-2-propanol			320	Benner <b>et al</b> , 2008
Resorcinol	9.8	2	. $3 \times 10^5$	Hoigné & Bader, 1983b
Salicylic acid	3.0,13.4		, 500	Hoigné & Bader, 1983b
anion			$2.8 \times 10^4$	Hoigné & Bader, 1983b
Tetracycline		7	$1.9 \times 10^6$	Dodd, 2008
Toluene			14	Hoigné & Bader, 1983a
Tonalide (AHTN)			8	Nöthe <b>et al</b> , 2007
2,4,6-Tribromoanisole			0.02	Peter & von Gunten, 2007
2,4,6-Trichloroanisole			0.06	Peter & von Gunten, 2007
1,2,3-Trichlorobenzene			, 0.06	Yao & Haag, 1991
2,4,5-Trichlorophenol	6.9		, 3000	Hoigné & Bader, 1983b
anion			. 1 × 10 <sup>9</sup>	Hoigné & Bader, 1983b
2,4,6-Trichlorophenol	6.1		$1 \times 10^4$	Hoigné & Bader, 1983b
anion			. 1 × 10 <sup>8</sup>	Hoigné & Bader, 1983b
Triclosan	8.1		$1.3 \times 10^3$	Suarez <b>et al</b> , 2007
		7	$3.8 \times 10^{7}$	Suarez <b>et al</b> , 2007
anion			$5.1 \times 10^8$	Suarez <b>et al</b> , 2007
2,4,6-Triiodophenol anion			$6.8 \times 10^6$	Mvula & von Sonntag, 2003
1,3,5-Trimethoxybenzene			$9.4 \times 10^5$	Muñoz & von Sonntag, 2000
3,4,5-Trimethoxytoluene			$2.8 \times 10^5$	Dodd <b>et al</b> , 2006a
1,2,4-Trimethylbenzene			400	Hoigné & Bader, 1983b
1,3,5-Trimethylbenzene			700	Hoigné & Bader, 1983b
Vancomycin		7	$6.1 \times 10^5$	Dodd, 2008
<b>m</b> -Xylene			94	Hoigné & Bader, 1983b
-Xylene			90	Hoigné & Bader, 1983b
-Xylene			140	Hoigné & Bader, 1983b

<sup>\*</sup>Consumption of substrate

### Aromatic compounds

In their pioneering work, Hoigné and Bader have shown that the logarithm of the rate constant for the reaction of ozone with substituted benzenes correlates linearly with the  $_{\rm p}$  values of the substituents (Hoigné & Bader, 1983a). As the value (slope) of this Hammett-type plot was negative ( 3.14), they concluded that in its reaction with benzene and its derivatives, ozone must act as an electrophilic agent. A similar plot with another set of  $_{\rm p}$  values also including the strongly electron-withdrawing NO<sub>2</sub> substituent is shown in Figure 7.1 (Naumov & von Sonntag, 2010). Here, the slope ( 2.65) is slightly less negative, but such variations are common when using different sets of values.



igure . Hammett-type plot for ozone reactions with benzene and its derivatives according to Naumov & von Sonntag, 2010 with permission. Logarithm of the rate constant vs. the  $_{\rm p}$  values taken from Gordon & Ford, 1972.

The first step in the reaction of ozone with aromatic compounds is the formation of an adduct [reaction (1)].

Hammett type plots are based on free energy relationships ( $G^0$  In K  $\times$  RT), and thus the standard Gibbs free energy of the formation of ozone adducts that can be calculated by quantum chemistry (Naumov & von Sonntag, 2010) must also correlate with the logarithm of the rate constant when the transition state is close to the adduct. This is apparently the case (Figure 7.2).

In the case of alkenes and alkynes, the ozone reaction seems to proceed via a concerted cycloaddition to the ozonide and ozone adducts cannot be calculated as intermediates (Chapter 6). In aromatic systems, however, the positive charge that develops upon formation of the ozone adduct [reaction (1)] is distributed over the whole aromatic ring, and a collapse to the ozonide [reaction (2)] is sufficiently retarded to allow an ozone adduct to become a distinct chemical entity (intermediate). This explains why

Aniline has also been included in Figure 7.1. Apparently, its ozone chemistry, as poorly as it is understood at present (Chapter 8), seems to be largely governed by an ozone addition to the ring. The yields of products that require an ozone addition to nitrogen are very minor.

Hammett plots are not only of academic interest; they are of high predictive value since—values are additive and this allows the estimation of an unknown rate constant. Figure 7.5 demonstrates that the second order rate constant for triclosan (for structure see Paragraph 7.4) could be derived by a Hammet-type correlation with substituted phenols for both the neutral and anionic form. The measured values correspond nicely with the predictions.

In another study, it has been shown for two musk fragrances, with the same molecular weight but different structure, galaxolide and tonalide (for their structures see Paragraph 7.4), that this approach can be successful within a factor of two (Nöthe et al., 2007). While galaxolide has only electron-donating substituents, tonalide also has an electron-withdrawing one, the acetyl group. As a consequence, the ozone reactivity of the latter is much lower (Table 7.1).

The rate constants for the reaction of benzene and all its mono-substituted derivatives with ozone is  $_{1}$ ,  $_{2}$  × 10 $^{3}$  M  $^{1}$  s  $^{1}$ . Muconic products that arise from the breakdown of the ozonide [cf. reaction (6)] react with rate constants near 10<sup>4</sup> M <sup>1</sup> s <sup>1</sup> (Chapter 6). Thus, a detailed study of the primary products is not feasible. Although phenol has a rate constant of only  $1.3 \times 10^3 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$ , the presence of low phenolate equilibrium concentrations [pK<sub>a</sub>(phenol) 9.9, k(phenolate  $O_3$ ) 1.4 x  $10^9 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$ ] results in the observed rate constant of .  $1 \times 10^6 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$  at pH 7 (for the reactivity pK see Chapter 2, Figure 2.3). Thus, phenols are good candidates for product studies. Upon substitution with two or more alkoxyl groups, the ozone rate constant is also enhanced to an extent, that a study of the primary products can be successful. Thus, our knowledge of the ozonolysis of aromatic compounds can be based only on electron-rich benzene derivatives, phenol (Mvula & von Sonntag, 2003; Ramseier & von Gunten, 2009), and di- and trimethoxybenzenes (Mvula et al., 2009). Here, it must be noted that in these compounds the high electron density in the benzene ring will allow reactions to occur that are not as likely to take place in the parent benzene and in benzene derivatives with electron-withdrawing substituents. With this caveat in mind, the ozone chemistry of aromatic compounds is discussed. The key reactions that were observed with such electron-rich aromatic compounds are presented here in general terms and will be substantiated below when discussing real systems.

A reaction that always occurs with aromatic compounds, and is well-documented in the reactions of olefins with ozone, is the formation of an ozonide and its breakdown [reactions (4) (7)].

### Chemistry of Ozone in Water and Wastewater Treatment

Table . Singlet oxygen yields in percentage of consumed ozone from the reaction of ozone with aromatic compounds according to (Muñoz **et al** , 2001). Aniline derivatives, discussed in Chapter 8, are included

ompound	Singlet o ygen yield/
Phenol pH 1.8	Nil
Phenol pH 7	6
Phenol pH 9	9
Tyrosine pH 7	9
2,4,6-Trimethylphenol pH 9	17
Pentachlorophenol pH 8	58
Pentabromophenol pH 8	48
2,4,6-Triodophenol pH 9	19
1,4-Dimethoxybenzene	6
1,3,5-Trimethoxybenzene	30
, -Dimethylaniline pH 8.5	7
, , , -Tetramethylphenylenediamine pH 3.5	9
, , -Tetramethylphenylenediamine pH 6	6

The decay of the ozone adduct into superoxide and phenoxyl radicals has also been suggested [reactions (15) and (16)] (Ragnar et al., 1999a, b).

 $O_3^{\dagger}$  and  $O_2^{\dagger}$  are the precursors of  ${}^{\dagger}OH$ , which may be formed in substantial yields in ozone reactions with aromatic compounds. Here,  $O_2^{\dagger}$  seems to be of a minor importance (see below). The  ${}^{\dagger}OH$  radical yield (with respect to ozone consumption formed in the ozone treatment of wastewater will also arise mainly from such reactions (Chapter 3). Moreover, the hydroxylation process generates further electron-rich aromatic compounds, a requirement for a continuation of  ${}^{\dagger}OH$  production at high ozone doses.

Phenols react very rapidly with ozone (Table 7.1), and in the reactions of ozone with aromatic compounds of relatively low reactivity (see above) they can build up to only very low steady-state concentrations and their formation may be difficult to detect.

. . Metho ylated ben enes

The products and yields formed upon ozonolysis of anisole, 1,2-dimethoxybenzene, 1,4-dimethoxybenzene and 1,3,5-trimethoxybenzene are compiled in Table 7.4. The structures of the products are shown in Figure 7.6.

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igure . Structures identified in the ozonolysis of anisole (1 3), 1,2-dimethoxybenzene (4), 1,4-dimethoxybenzene (5–9) and 1,3,5-trimethoxybenzene (10–12).

Its ensuing decay routes are discussed in some detail in Mvula et al. (2009). Here it suffices to show only the essentials [reactions (19) (25)], that is, neglecting acid/base equilibria. As in olefins, there is decay into the ozonide [reaction (19)]. This is the precursor of muconic compound 12 [reaction (20)]. In competition, the adduct may release  $O_3^{\dagger}$  [reaction (21)], the origin of the relatively high  $^{\dagger}OH$  yield  $(O_3^{\dagger}H_2O)^{\dagger}OH)$  O2 OH, details in Chapter 11). The release of singlet oxygen [reaction (22)], is connected with a hydroxylation of the aromatic ring [formation of 11, reaction (23)]. Reaction (24) gives rise to  $O_2^{\dagger}$  and reaction (25) to a hydrotrioxide.

A major product is quinone 10 (Table 7.4). It has been suggested that it is mainly formed upon the decay of the hydrotrioxide [reactions (26) (28)]. For the reaction of  $HO_2^{\dagger}/O_2^{\dagger}$  with phenoxyl radicals [cf. reaction (27)] see Jin et al. (1993).

$$\begin{array}{c} O-CH_{3} \\ O-O-O-OH \\ O-CH_{3} \\ O-CH$$

### . . Phenols

Phenols react moderately rapidly with ozone, but the reaction of their anions is close to diffusion controlled (Table 7.1). With  $pK_a(phenol)$  9.9, the rate of reaction observed at pH 7 is hence determined by the reaction of the phenolate anion in equilibrium (Chapter 2). Nevertheless, the product yields listed in Table 7.5 for pH 6 7 and for pH 10 are markedly different in many cases and must be due to different decay routes of the primary ozone adduct at these two different pH conditions.

Table . Ozonolysis of phenol. Products and their yields in percentage of ozone consumed. In several experiments, tertiary butanol (tBuOH) was added for scavenging <sup>†</sup>OH radicals. When more than one value is given, further runs at four or five different ozone concentrations were carried out Mvula & von Sonntag (2003)

Product Scavenger	<b>≤</b> p	р	р
Hydroquinone	1.6/1.1 <sup>(a)</sup>	13.3/16	0.8
Hydroquinone (tBuOH)	ND	, 1	ND
Catechol	4.8/1.8 <sup>(a)</sup>	13.6	20
Catechol (tBuOH)	ND	2	ND
1,4-Benzoquinone	9.6/10.4/6.1 <sup>(a)</sup>	4.6/4.6	32
1,4-Benzoquinone (tBuOH)	ND	13	ND
s, s-Muconic acid	4.8/4.0/3 <sup>(a)</sup>	2.8	1
s, s-Muconic acid (tBuOH)	ND	2.0	ND
4,4 -Dihydroxybiphenyl	ND	ND	1
2,4 -Dihydroxybiphenyl	ND	ND	1
Singlet dioxygen	absent	5.6	8
<sup>†</sup> OH (estimated)	20/22	28/26/24	22
Nitroform anion (TNM)	3	ND	ND
Organic (hydro)peroxide	ND	absent	ND
Organic (hydro)peroxide (tBuOH)	ND	2.6	ND
Hydrogen peroxide	8.5	4.8	2
Hydrogen peroxide (tBuOH)	ND	16	ND
Hydrogen peroxide (DMSO)	ND	13	ND
Phenol consumption	33 <sup>(a)</sup>	48 <sup>(a)</sup>	59 <sup>(a)</sup>
Phenol consumption (tBuOH)	ND	42 <sup>(a)</sup>	ND

 $<sup>^{(</sup>a)}$ [Phenol] 2.5 x 10  $^4$  M, ND not determined, TNM tetranitromethane, DMSO dimethyl sulfoxide.

With hydroquinone as substrate, the yield of 1,4-benzoquinone is markedly enhanced in the presence of tBuOH and the data shown in Table 7.7 are supported by the study of Ramseier & von Gunten (2009), which gives a hydroquinone consumption related value of 83% at pH 7 and 52 61% at pH 3. The corresponding oxidation product of catechol, 1,2-benzoquinone, is unstable and would escape detection (cf. Table 7.8).

Table . Ozonolysis of hydroquinone (1 mM). Products and their yields in percentage of ozone consumed in absence and presence of tBuOH, added for scavenging  $^{\dagger}$ OH (Mvula & von Sonntag, 2003)

Product	ield
1,4-Benzoquinone	13/12
1,4-Benzoquinone (t-BuOH)	36/32
1,4-Benzoquinone (DMSO)	30
2-Hydroxy-1,4-benzoquinone	11
2-Hydroxy-1,4-benzoquinone (tBuOH)	, 1
2-Hydroxy-1,4-benzoquinone (DMSO)	, 1
1,2,4-Trihydroxybenzene	absent
Singlet dioxygen	16
Hydrogen peroxide	5.6
Hydrogen peroxide (tBuOH)	14
Hydrogen peroxide (DMSO)	10.4
Organic (hydro)peroxides	absent
Organic (hydro)peroxides (tBuOH)	1.9
Formaldehyde	absent
Formaldehyde (tBuOH)	21/20
2-Hydroxy-2-methylpropionaldehyde	absent
2-Hydroxy-2-methylpropionaldehyde (tBuOH)	23
Methanesulfinic acid (DMSO)	6
Methanesulfonic acid (DMSO)	27
Hydroquinone consumption	47 <sup>(a)</sup>
Hydroquinone consumption (tBuOH)	48 <sup>(a)</sup>

 $<sup>^{\</sup>rm (a)}[{\rm Hydroquinone}]~~2.5$  x 10  $^4$  M, TNM ~ tetranitromethane, DMSO dimethyl sulfoxide.

cis,cis-Muconic acid is formed via the ozonide [cf. reaction (4) (6)]. The hydroxyhydroperoxide that must be the intermediate typically loses  $H_2O_2$  [reaction (35)], but here a water elimination is observed [reaction (36)]. This has been attributed to the fact that reaction (35) is reversible, while reaction (36) is not (Mvula & von Sonntag, 2003).

respectively. Details of the preferred sites of attack as a function of pH are not fully established, but these functions and the enolic groups are obvious candidates.

Amoxillin has three ozone-reactive sites, the phenol, amine and sulfide groups. It has  $pK_a$  values at 2.68 (carboxylic acid), 7.49 (amine) and 9.68 (phenol). Rate constants as a function of pH have not been reported, but it is most likely that at the pH values relevant for water ozonation, amoxillin degradation by ozone is largely governed by reactions with the deprotonated phenol site in equilibrium (Andreozzi et al., 2005). The amine (Chapter 8) and sulfide (Chapter 9) sites would react more slowly.

Aflatoxins belong to the group of mycotoxins which are produced by a number of fungi such as Aspergillus, Penicillum and Fuscarum. The structures of the most abundant ones are shown below. Their aromatic rings carry strongly electron-donating substituents, that is, their rate constants toward ozone must be high, most likely close to that of 1,3,5-trimethoyxbenzene (Table 7.1). As a consequence, they are readily degraded (detoxified) by ozone (McKenzie et al., 1997). Their olefinic functions are all deactivated by electron-withdrawing substituents (Chapter 6), and thus their contributions to detoxifications by ozone are expected to be minor.

Naphthalene sulfonic acid derivatives are used as textile auxiliaries. Some aspects of their degradation by ozone have been addressed (Babuna et al., 2009). The reaction of ozone with such compounds is moderately fast, near 10<sup>3</sup> M <sup>1</sup> s <sup>1</sup>, if the parent, naphthalene, is a good guide (Table 7.1). Naxopren is an antiphlogistic pharmaceutical with a naphthalene moiety, additionally activated by a methoxy and an alkyl group. This leads to a marked enhancement of the rate constant (Table 7.1) (Huber et al., 2005).

The lipid-lowering drug gemfibrozil contains a benzene ring that is activated by two alkyl and one alkoxyl groups. Its ozone rate constant has been estimated to  $2 \times 10^4 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$ , by quantitative structure activity relationship (QSAR) (Lee & von Gunten, 2012), which lies between naxopren and bezafibrate (Table 7.1). The herbicide methoxychlor also belongs to the group of aromatic compounds activated by alkoxyl groups.

## Chapter 8

# Nitrogen-containing compounds

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For aliphatic amines to be ozone-reactive, the lone electron pair at nitrogen has to be accessible. Protonation of aliphatic amines or complexation of the nitrogens as in Fe(III) EDTA or Fe(III) DTPA eliminates the ozone reactivity or at least strongly reduces it (Table 8.1).

Table . Compilation of ozone rate constants of nitrogen-containing compounds in aqueous solution. Rate constants for sulfur-containing amino acids are given in Chapter 9. Published rate constants are rounded to significant figures

ompound	p K <sub>a</sub>	р	k/M s	eference
Acebutolol	9.2		2.9 <b>x</b> 10 <sup>5</sup>	Benner <b>et al</b> ., 2008
		7	$1.9 \times 10^3$	Benner et al., 2008
protonated			60	Benner et al., 2008
-Acetylglycine		3.7	0.3	Pryor <b>et al</b> ., 1984
Acetylhistidine	7.3		$8.4 \times 10^5$	Pryor <b>et al</b> ., 1984
Acetyllysine	10.5		$1.0 \times 10^5$	Pryor <b>et al</b> ., 1984
Acetyllysine	9.46		$2.4 \times 10^4$	Pryor <b>et al</b> ., 1984
protonated			no reaction	Pryor <b>et al</b> ., 1984
(4)-Acetylsulfamethoxazole	5.5		260	Dodd <b>et al</b> ., 2006a
protonated			20	Dodd <b>et al</b> ., 2006a
Alachlor			3.4	de Laat <b>et al</b> ., 1996
Alanine	9.87		$6.4 \times 10^4$	Hoigné & Bader, 1983b
			$7.6 \times 10^4$	Pryor <b>et al</b> ., 1984
			$2.8 \times 10^4$	Muñoz & von Sonntag, 2000b
protonated			no reaction	Pryor <b>et al</b> ., 1984
			$3 \times 10^{-3}$	Hoigné & Bader, 1983b
-Alanine			$6.2 \times 10^4$	Hoigné & Bader, 1983b

ntn e )

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Table . Compilation of ozone rate constants of nitrogen-containing compounds in aqueous solution. Rate constants for sulfur-containing amino acids are given in Chapter 9. Published rate constants are rounded to significant figures ( **ntn e** )

ompound	$pK_a$	р	k/M s	eference
Amikacin	6.7, 8.4	7	$1.8 \times 10^3$	Dodd, 2008
	8.4, 9.7			
4-Aminophenylmethyl sulfone			$4.7 \times 10^4$	Dodd <b>et al</b> ., 2006a
Ammonia	9.24		20	Hoigné & Bader, 1983b
			44	Garland <b>et al</b> ., 1980
protonated			no reaction	Hoigné & Bader, 1983b
Aniline	4.63		$9.0 \times 10^7$	Hoigné & Bader, 1983
			$3.8 \times 10^7$	Tekle-Röttering et al., 2011
		6.5	$1.4 \times 10^7$	Pierpoint et al., 2001
		1.5	$5.9 \times 10^4$	Pierpoint et al., 2001
Arginine	8.99		$5.7 \times 10^4$	Pryor <b>et al</b> ., 1984
Asparagine monoanion	2.0, 8.8		$4.2 \times 10^5$	Pryor <b>et al</b> ., 1984
Aspartate ion	9.82		$4.1 \times 10^4$	Pryor <b>et al</b> ., 1984
protonated			1.0	Pryor <b>et al</b> ., 1984
Atenolol	9.6		$6.3 \times 10^5$	Benner et al., 2008
protonated			110	Benner et al., 2008
Atrazine		2	24	Yao & Haag, 1991
			2.3	Xiong & Graham, 1992
			5.65	de Laat <b>et al</b> ., 1996
			6.0	Acero <b>et al</b> ., 2000
Azithromycin	8.7, 9.5	7	$1.1 \times 10^5$	Dodd <b>et al</b> ., 2006a
Azobenzene		2	220	Yao & Haag, 1991
1-(2-Benzaldehyde)-4-hydro(1 ,3 )- quinazoline-2-one			3.0	Kosjek <b>et al</b> , 2009
Benzotriazole	1.6, 8.2		35	Lutze <b>et al</b> ., 2011a
			36	Vel Leitner & Roshani, 2010
anion			2650	Lutze <b>et al</b> ., 2011a
Benzylamine	9.33		$6.3 \times 10^4$	Pryor <b>et al</b> ., 1984
Butylamine	10.77		$1.2 \times 10^5$	Pryor <b>et al</b> ., 1984
			$1.7 \times 10^5$	Hoigné & Bader, 1983b
protonated			0.1	Pryor <b>et al</b> ., 1984
<b>s</b> -Butylamine	10.83		$5.2 \times 10^4$	Pryor <b>et al</b> ., 1984
protonated			no reaction	Pryor <b>et al</b> ., 1984
3-Chloroaniline		6	$7.84 \times 10^6$	Pierpoint et al., 2001
4-Chloroaniline		6	$1.04 \times 10^7$	Pierpoint et al., 2001
5-Chlorobenzotriazole	0.04, 7.5		13	Lutze et al., 2011a
anion			630	Lutze <b>et al</b> ., 2011a

( **ntn e** )

## Nitrogen-containing compounds

Table . Compilation of ozone rate constants of nitrogen-containing compounds in aqueous solution. Rate constants for sulfur-containing amino acids are given in Chapter 9. Published rate constants are rounded to significant figures ( **ntn e** )

ompound	$pK_a$	р	k/M s	eference
Chlorotoluron			50.5	de Laat <b>et al</b> ., 1996
			394	Benitez <b>et al</b> ., 2007
Ciprofloxacin	6.2, 8.8		9 <b>x</b> 10 <sup>5</sup>	Dodd <b>et al</b> ., 2006a
monoprotonated			$7.5 \times 10^3$	Dodd et al., 2006a
Clarithromycin		7	$4 \times 10^4$	Lange <b>et al</b> ., 2006
Creatine		2	0.5	Hoigné & Bader, 1983b
Creatinine		6	2	Hoigné & Bader, 1983b
Cyclohexanemethylamine	10.3		$7.1 \times 10^4$	Dodd <b>et al</b> ., 2006a
protonated			, 1	Dodd et al., 2006a
Cyclohexylamine	10.6		$4.9 \times 10^4$	Dodd <b>et al</b> ., 2006a
protonated			, 1	Dodd <b>et al</b> ., 2006a
Cyclophosphamide			2.27	Fernández <b>et al</b> ., 2010
			3.0	Garcia-Ac <b>et al</b> ., 2010
Deethylatrazine		2	0.18	Acero <b>et al</b> ., 2000
Deethyldeisopropylatrazine		2	, 0.1	Acero <b>et al</b> ., 2000
Deisopropylatrazine		2	3.1	Acero <b>et al</b> ., 2000
2,4-Diamino-5-methylpyrimidine	3.2, 7.1		$1.3 \times 10^6$	Dodd <b>et al</b> ., 2006a
monoprotonated			$2.9 \times 10^{3}$	Dodd <b>et al</b> ., 2006a
diprotonated			$5.0 \times 10^2$	Dodd <b>et al</b> ., 2006a
1,4-Diazabicyclo[2.2.2]octane (DABCO)	3.0, 8.2		$3.2 \times 10^6$	Muñoz & von Sonntag, 2000b
monoprotonated			$3.5 \times 10^{3}$	Muñoz & von Sonntag, 2000b
Diazepam			0.75	Huber <b>et al</b> , 2003
Dichloramine			1.3	Haag & Hoigné, 1983b
Diclofenac			$1.8 \times 10^4$	Vogna <b>et al</b> ., 2004
			$6.8 \times 10^5$	Sein <b>et al</b> ., 2008
			10 <sup>6</sup>	Huber <b>et al</b> ., 2003
Diethylamine	10.49		$6.2 \times 10^5$	Pryor <b>et al</b> ., 1984
			$9.1 \times 10^5$	Muñoz & von Sonntag, 2000b
protonated			11 + 6	Pryor <b>et al</b> ., 1984
Diethylenetriaminepentaacetic acid	0.1, 0.7			
(DTPA)	1.6, 2.0			
	2.6, 4.3			
	8.6, 10.5			
CaDTPA <sup>3</sup>			6200	Stemmler et al., 2001
Fe(III)DTPA <sup>2</sup>			, 10	Stemmler et al., 2001
Fe(III)(OH)DTPA <sup>3</sup>			$2.4 \times 10^5$	Stemmler et al., 2001

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respectively. Details of the preferred sites of attack as a function of pH are not fully established, but these functions and the enolic groups are obvious candidates.

Amoxillin has three ozone-reactive sites, the phenol, amine and sulfide groups. It has  $pK_a$  values at 2.68 (carboxylic acid), 7.49 (amine) and 9.68 (phenol). Rate constants as a function of pH have not been reported, but it is most likely that at the pH values relevant for water ozonation, amoxillin degradation by ozone is largely governed by reactions with the deprotonated phenol site in equilibrium (Andreozzi et al., 2005). The amine (Chapter 8) and sulfide (Chapter 9) sites would react more slowly.

Aflatoxins belong to the group of mycotoxins which are produced by a number of fungi such as Aspergillus, Penicillum and Fuscarum. The structures of the most abundant ones are shown below. Their aromatic rings carry strongly electron-donating substituents, that is, their rate constants toward ozone must be high, most likely close to that of 1,3,5-trimethoyxbenzene (Table 7.1). As a consequence, they are readily degraded (detoxified) by ozone (McKenzie et al., 1997). Their olefinic functions are all deactivated by electron-withdrawing substituents (Chapter 6), and thus their contributions to detoxifications by ozone are expected to be minor.

Naphthalene sulfonic acid derivatives are used as textile auxiliaries. Some aspects of their degradation by ozone have been addressed (Babuna et al., 2009). The reaction of ozone with such compounds is moderately fast, near 10<sup>3</sup> M <sup>1</sup> s <sup>1</sup>, if the parent, naphthalene, is a good guide (Table 7.1). Naxopren is an antiphlogistic pharmaceutical with a naphthalene moiety, additionally activated by a methoxy and an alkyl group. This leads to a marked enhancement of the rate constant (Table 7.1) (Huber et al., 2005).

The lipid-lowering drug gemfibrozil contains a benzene ring that is activated by two alkyl and one alkoxyl groups. Its ozone rate constant has been estimated to  $2 \times 10^4 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$ , by quantitative structure activity relationship (QSAR) (Lee & von Gunten, 2012), which lies between naxopren and bezafibrate (Table 7.1). The herbicide methoxychlor also belongs to the group of aromatic compounds activated by alkoxyl groups.

## Chapter 8

## Nitrogen-containing compounds

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For aliphatic amines to be ozone-reactive, the lone electron pair at nitrogen has to be accessible. Protonation of aliphatic amines or complexation of the nitrogens as in Fe(III) EDTA or Fe(III) DTPA eliminates the ozone reactivity or at least strongly reduces it (Table 8.1).

Table . Compilation of ozone rate constants of nitrogen-containing compounds in aqueous solution. Rate constants for sulfur-containing amino acids are given in Chapter 9. Published rate constants are rounded to significant figures

ompound	p K <sub>a</sub>	р	k/M s	eference
Acebutolol	9.2		2.9 <b>x</b> 10 <sup>5</sup>	Benner <b>et al</b> ., 2008
		7	$1.9 \times 10^3$	Benner et al., 2008
protonated			60	Benner et al., 2008
-Acetylglycine		3.7	0.3	Pryor <b>et al</b> ., 1984
Acetylhistidine	7.3		$8.4 \times 10^5$	Pryor <b>et al</b> ., 1984
Acetyllysine	10.5		$1.0 \times 10^5$	Pryor <b>et al</b> ., 1984
Acetyllysine	9.46		$2.4 \times 10^4$	Pryor <b>et al</b> ., 1984
protonated			no reaction	Pryor <b>et al</b> ., 1984
(4)-Acetylsulfamethoxazole	5.5		260	Dodd <b>et al</b> ., 2006a
protonated			20	Dodd <b>et al</b> ., 2006a
Alachlor			3.4	de Laat <b>et al</b> ., 1996
Alanine	9.87		$6.4 \times 10^4$	Hoigné & Bader, 1983b
			$7.6 \times 10^4$	Pryor <b>et al</b> ., 1984
			$2.8 \times 10^4$	Muñoz & von Sonntag, 2000b
protonated			no reaction	Pryor <b>et al</b> ., 1984
			$3 \times 10^{-3}$	Hoigné & Bader, 1983b
-Alanine			$6.2 \times 10^4$	Hoigné & Bader, 1983b

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